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# *Studies of mineral sulpho-salts: XIII—Polybasite and pearceite.*[1]

(With Plates I and II.)

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THESE two minerals are analogous silver compounds with similar pseudo-hexagonal monoclinic form and similar compositions: polybasite, $8(Ag,Cu)_2.(Sb,As)_2S_3$, and pearceite, $8(Ag,Cu)_2S.As_2S_3$. Cu replaces Ag in considerable and varying amounts in both minerals, and in polybasite there may also be substantial replacement of Sb by As. However, the rather numerous existing analyses do not indicate continuous chemical variation from arsenian polybasite to pearceite, and therefore it is proper to recognize the two minerals as distinct species rather than end-members of a series.

Although most of the specific properties of polybasite and pearceite are known (Dana, 7th edition, 1944, pp. 351–355), there are still some gaps and uncertainties in the descriptions. The occasion to study these minerals was offered by some sharply crystallized polybasite from British Columbia, kindly sent to us by Professor H. V. Warren; the work was carried out partly by the senior author in the University of Toronto and partly by the junior author in Queen's University, Kingston, Ontario.

[1] For the preceding paper of this series see E. W. Nuffield (1946) [M.A. **10**–15]. No. II by L. G. Berry on jamesonite appeared in this Magazine, 1940, vol. 25, pp. 597–608.

The material brought together for the present study consisted of the specimens listed below. In this list the collections are indicated as follows: UT (University of Toronto, Department of Geological Sciences); ROM (Royal Ontario Museum of Geology and Mineralogy; specimen kindly loaned by Dr. V. B. Meen); QU (Queen's University, Department of Mineralogy). Specimen no. 4 was kindly presented by Dr. M. H. Frohberg.

1. Polybasite, Highland Bell mine, Beaverdell, Greenwood mining division, British Columbia (UT, R 151); groups of sharp, bright, intergrown, tabular crystals up to 10 mm. wide.

2. Polybasite, Keeley mine, South Lorrain, Ontario (ROM, M 14781). Boxwork of imperfect plates, occasionally thin enough to transmit red light, with minute adhering octahedra of argentite, emplanted on massive radial-fibrous safflorite.

3. Polybasite, Cobalt, Ontario (QU); thin, dark ruby-red hexagonal plates on massive white arsenides.

4. Polybasite, Yankee Boy mine, Ouray County, Colorado (QU); isolated dull hexagonal plates with quartz and galena.

5. Polybasite, Las Chiapas mine, Sonora, Mexico (UT, R 257); massive crystallized polybasite with attached pyrargyrite and a drusy coating of chalcopyrite.

6. Pearceite, Aspen, Colorado (QU); intergrowth of rough, dull black hexagonal plates.

7. Pearceite, Silver, Montana (ROM, E 2768); a few black crystal chips.

## POLYBASITE

*Physical properties.*—In all our specimens polybasite shows a marked tendency to develop the characteristic pseudo-hexagonal tabular form, with strong triangular terracing on the basal planes, much oscillatory development of the edge-faces, and intimate subparallel to irregular intergrowth of the crystal plates. The colour is iron-black and the crystals are opaque except in thin splinters which are dark red. The lustre is sub-metallic or adamantine to dull, and the mineral is remarkably brittle, a property which is appropriately expressed in Werner's name *Sprödglaserz* (which included polybasite and stephanite), and the name *Brittle Silver* used by Colorado miners (Penfield, 1896), but is not mentioned in Dana (1944). The basal cleavage is difficult but yields plane-faced fragments.

New specific gravity measurements on polybasite, made with the Berman balance, are compared below with recently published values:

| | Sp. gr. | |
|---|---|---|
| Beaverdell (material no. 1) ... ... ... ... | 6·30 | R. M. Thompson |
| Beaverdell (veinlets) ... ... ... .... ... | 6·26 | Staples & Warren (1946, p. 31) |
| Beaverdell (coatings) ... ... ... ... ... | 6.28 | |
| Beaverdell (crystal fragments) ... ... ... ... | 6·33 | |
| South Lorrain (material no. 2) ... ... ... ... | 6·27 | R. M. Thompson |
| Sonora (material no. 5) ... ... ... ... ... | 6·27 | L. G. Berry |

Polished sections of the materials from Beaverdell and South Lorrain were examined by R. M. Thompson who noted physical, optical, and etch properties in agreement with those given by Short (1940, p. 128).

*Crystal form.*—Good crystal form and bright faces were shown by a single crystal of polybasite from the Highland Bell mine (material no. 1). This crystal is an incomplete hexagonal tablet about 2 mm. wide, bevelled by numerous bright faces most of which gave good reflections. With an excellent basal plane taken as the pole-face on the two-circle goniometer the edge-faces all lie in three radial zones, and the resulting projection shows no significant deviation from hexagonal symmetry. Later X-ray work confirmed the monoclinic symmetry of polybasite, but no way was found to distinguish the quasi-equivalent (*h*0*l*) and (*hhl*) zones on the relatively large measured crystal, which has therefore been arbitrarily placed in one of the alternative positions (text-fig. 1). The angles measured on this crystal are compared in table I with angles calculated for polybasite on Penfield's elements (Dana, 1944, p. 351):

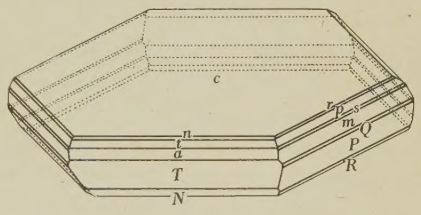


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FIG. 1. Polybasite: measured crystal from Highland Bell mine, Beaverdell, B.C.

$$a : b : c = 1{\cdot}7309 : 1 : 1{\cdot}5796\,;\ \beta = 90°\ 00'.$$

TABLE I. Polybasite: Measured and calculated angles.

| Form. | Measured. | | Calculated. | |
|---|---|---|---|---|
| | $\phi$ | $\rho$ | $\phi$ | $\rho$ |
| *c*(001) ... ... ... | — | 0°00′ | — | 0°00′ |
| *a*(100) ... ... ... | 90°00′ | 89 56 | 90°00′ | 90 00 |
| *m*(110) ... ... ... | 29 55 | 89 50 | 30 01 | 90 00 |
| *n*(101) ... ... ... | 90 00 | 42 09 | 90 00 | 42 23 |
| *N*($\bar{1}$01) ... ... ... | −90 00 | 42 08 | −90 00 | 42 23 |
| *t*(201) ... ... ... | 90 00 | 61 09 | 90 00 | 61 17 |
| *T*($\bar{2}$01) ... ... ... | −90 00 | 61 06 | −90 00 | 61 17 |
| *r*(112) ... ... ... | 29 55 | 42 08 | 30 01 | 42 22 |
| *R*($\bar{1}$12) ... ... ... | −30 01 | 42 11 | −30 01 | 42 22 |
| *p*(111) ... ... ... | 29 55 | 61 12 | 30 01 | 61 16 |
| *P*($\bar{1}$11) ... ... ... | −30 01 | 61 14 | −30 01 | 61 16 |
| **Q*($\bar{4}$43) ... ... ... | −30 01 | 67 48 | −30 01 | 67 39½ |
| *s*(221) ... ... ... | 29 55 | 75 02 | 30 01 | 74 40½ |

*New form.

These observations agree well with those of Penfield and they confirm the uncommon form $a(100)$ and establish the form $Q(\bar{4}43)$ which was observed as a good face. A terraced plate from South Lorrain (material no. 2) gave *ca* or *cm* = 89° 16′–89° 57′ (calc. 90° 00′), *co* = (001) (114) = 23° 15′–25° 05′ (calc. 24° 31′). An incomplete crystal from Sonora (material no. 5) gave *cn* or *cr* = 42° 27′ (calc. 42° 23′), *ct* or *cp* = 60° 58′ (calc. 61° 16′).

*Optics.*—Efforts to add to the incomplete optical data for polybasite were largely unsuccessful. Extremely thin basal plates transmit cherry-red light and occasionally show a poor acute bisectrix figure with small optic axial angle. More often even thin basal plates fail to extinguish between crossed nicols and they yield no useful interference-figure. This suggests lamellar twinning about the axis [110] with composition on (001), as in other minerals with pseudo-hexagonal layer-structures. An attempt to determine the refractive indices in melts of selenium and arsenic selenide likewise failed owing to the apparent solution of the mineral in the melts. Finally, an effort was made to measure a refractive index by finding the angle of incidence of reflected light showing maximum polarization; but, although the base of the measured crystal served well as a reflecting plane on the goniometer, a position of maximum polarization could not be sharply recognized with a suitably placed nicol prism.

*Unit cell.*—The unit cell of polybasite has been determined only once, by Gossner & Kraus (1934), who gave partly unsatisfactory data on unanalysed material from Guanajuato, Mexico. In view of the chemical variation in polybasite the unit cell was determined on all the available materials, from single-crystal X-ray photographs. For this purpose minute relatively thick crystals or basal cleavage plates were rotated about the cleavage normal [001] and about one or other of the edges [010] or [110], and rotation and zero-layer Weissenberg photographs were taken. The rotation photographs about [001] all showed a strong set of layer-lines giving a period of about 12 kX and in all crystals, except that from Sonora, faint intermediate layer-lines requiring the double period of about 24 kX. The Weissenberg resolutions of the layer ($hk0$) showed perfectly hexagonal symmetry of the spots as regards position, but some exceptions as regards intensity. The rotation photographs about [010] or [110] on the different specimens are all alike, showing a strong set of layer-lines requiring a period of about 7·5 kX and a weaker but very clear set of intermediate layer-lines giving a period of about 15 kX (pl. I, fig. 1).

The zero-layer Weissenberg photographs about [010] or [110] are

interesting in affording direct proof of the symmetry of polybasite. The spots ($h0l$) and ($\bar{h}0l$), or ($hhl$) and ($\bar{h}\bar{h}l$), are exactly symmetrical in position about the row ($00l$), but they are clearly not symmetrical in intensity (pl. II, fig. 6). The vertical axis is therefore not an even-fold symmetry-axis; and, since trigonal symmetry is excluded by the optical behaviour, the symmetry cannot be higher than monoclinic.

The cell dimensions measured on polybasite are assembled below and compared with those of Gossner & Kraus (table II).

TABLE II. Polybasite: Comparison of cell dimensions (kX).

| | *a*. | *b*. | *c*. | *β*. |
|---|---|---|---|---|
| Beaverdell, B. C. (no. 1) ... ... | 26·12 | 15·08 | 23·89 | 90° 00′ |
| South Lorrain, Ont. (no. 2) ... ... | 26·12 | 15·08 | 23·84 | 90 00 |
| Cobalt, Ont. (no. 3) ... ... ... | 26·24 | 15·15 | 23·90 | 90 00 |
| Ouray, Colo. (no. 4) ... ... ... | 26·12 | 15·08 | 23·88 | 90 00 |
| Sonora, Mex. (no. 5) ... ... ... | 26·12 | 15·08 | 11·92 | 90 00 |
| Guanajuato, Mex. (Gossner & Kraus, 1934) ... ... ... ... ... | 12·99 | 7·50 | 11·95 | 90 — |

The new cell dimensions are practically constant, except for the halved *c*-period for no. 5 and the slightly larger values for no. 3, which may be relatively free from copper. The usual dimensions of polybasite are thus about double those of Gossner & Kraus, who noticed indications of a double *b*-period but wrongly attributed this to twinning.

The strictly missing spectra give the conditions: ($hkl$) present only with $(h+k)$ even, ($h0l$) present only with $h$ even, and ($h00$) present only with $h = 4n$. In addition, there are only weak exceptions to the further conditions: ($hkl$) present only with $l$ even, ($h0l$) present only with $h = 4n$ and $l$ even. These conditions are compatible with the holohedral space-group $C2/m$, but other space-groups are also possible.

The axial ratios from the new cell dimensions are compared below with the structural ratios of Gossner & Kraus and with the axial ratios previously obtained goniometrically by Penfield (1896) and Miers (1889).

TABLE III. Polybasite: Comparison of axial ratios.

| | *a* : *b* : *c* | *β* |
|---|---|---|
| Beaverdell, B. C. (no. 1) ... ... ... ... | 1·732 : 1 : 1·584 | 90° 00′ |
| South Lorrain, Ont. (no. 2) ... ... ... | 1·732 : 1 : 1·581 | 90 00 |
| Cobalt, Ont. (no. 3) ... ... ... ... | 1·732 : 1 : 1·579 | 90 00 |
| Ouray, Colo. (no. 4) ... ... ... ... | 1·732 : 1 : 1·584 | 90 00 |
| Sonora, Mex. (no. 5) ... ... ... ... | 1·732 : 1 : ½(1·581) | 90 00 |
| Guanajuato, Mex. (Gossner & Kraus, 1934) ... | 1·731 : 1 : 1·593 | 90 — |
| Ouray, Colo. (Penfield, 1896) ... ... ... | 1·7309 : 1 : 1·5796 | 90 00 |
| Several localities (Miers, 1889, corrected to suit his angles) ... ... ... ... ... | 1·7262 : 1 : 1·576 | (90 00) |

Except for the values of Gossner & Kraus, which are slightly out of line, the assembled values are remarkably constant, indicating that the geometrical form of polybasite varies but little with variation of the chemical composition.

*Analyses and cell contents.*—The measured cell dimensions and specific gravity of the polybasite from Beaverdell, B.C. (material no. 1) give the molecular weight of the unit-cell contents, $M = 35{,}929$. By combining this number with the analysis of this material in the usual way the atomic content of the unit cell is obtained (table IV). It will be

TABLE IV. Polybasite from Beaverdell, B.C.: Analysis and cell content, $M = 35{,}929$.

| | 1. | 2. | | 3. |
|---|---|---|---|---|
| Ag ... ... | 69·72 | 232·5 | 253·4 | 256 |
| Cu ... ... | 3·70 | 20·9 | | |
| Sb ... ... | 10·15 | 30·0 | 33·0 | 32 |
| As ... ... | 0·63 | 3·0 | | |
| S ... ... | 15·68 | 175·9 | 175·9 | 176 |
| | 99·88 | 462·3 | | 464 |

1. Analysis by R. N. Williams; sp.gr. 6·26. 2. Empirical cell contents. 3. Ideal cell contents.

observed that the ideal cell contents represent only a slight adjustment of the empirical cell contents, giving the formula:

$$Ag_{234}Cu_{22}Sb_{30}As_2S_{176} = 16[8(Ag,Cu)_2S.Sb_2S_3]$$

and the calculated density 6·33. Thus the Beaverdell polybasite conforms closely to the accepted composition $8(Ag,Cu)_2S.Sb_2S_3$, and represents material which is exceptionally low in Cu and As. The new cell dimensions require 16 formula weights, rather than 2 formula weights indicated by the pseudo-cell of Gossner & Kraus.

A full view of the chemical variation in polybasite is given in table V in which the seventeen available analyses have been expressed in terms of a sum of 29 atoms or 1/16 of the full unit cell, and arranged in order of decreasing number of Ag atoms. It will be seen that Cu ranges approximately from 1 to 4 atoms or from 1/16 to 1/4 of the (Ag,Cu) component. Arsenic varies more widely, from zero to over $\frac{1}{2}$ of the (Sb,As) component. The average totals of the components (Ag,Cu), (Sb,As), and S, excluding only the few values in parentheses, come very close to the ideal numbers, 16, 2, 11, respectively.

*X-ray powder pattern.*—The available samples of polybasite gave practically identical X-ray powder patterns, three of which are repro-

TABLE V. Polybasite: Analyses and cell contents.

| | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. |
|---|---|---|---|---|---|---|---|---|---|---|
| Ag ... | 70·97 | 72·01 | 69·72 | 68·55 | 69·80 | 68·90 | 69·99 | 68·39 | 67·13 | 67·95 |
| Cu ... | 2·50 | 3·36 | 3·70 | 3·36 | 4·25 | 5·21 | 4·11 | 5·13 | 2·23 | 6·07 |
| Fe ... | — | 0·34 | — | 0·14 | — | 0·09 | 0·29 | — | 0·31 | — |
| Zn ... | — | — | — | — | — | — | — | — | — | — |
| Pb ... | — | — | — | — | — | — | — | — | 2·41 | 0·76 |
| Bi ... | — | — | — | — | — | — | — | — | 0·80 | — |
| Sb ... | 9·46 | 5·46 | 10·15 | 11·53 | 10·72 | 8·85 | 8·39 | 10·64 | 9·50 | 5·15 |
| As ... | 2·37 | 3·41 | 0·63 | — | 0·58 | 1·07 | 1·17 | 0·50 | 0·78 | 3·88 |
| S ... | 14·69 | 15·87 | 15·68 | 15·55 | 15·57 | 15·33 | 16·35 | 15·43 | 16·94 | 16·37 |
| | 99·99 | 100·45 | 99·88 | 99·13 | 100·92 | 99·45 | 100·30 | 100·09 | 100·10 | 100·18 |
| Ag ... | 15·09 | 14·76 | 14·58 | 14·51 | 14·49 | 14·39 | 14·33 | 14·25 | 13·94 | 13·69 |
| Cu ... | 0·90 | 1·17 | 1·31 | 1·21 | 1·50 | 1·85 | 1·43 | 1·81 | 0·78 | 2·08 |
| Fe ... | — | 0·13 | — | 0·06 | — | 0·03 | 0·11 | — | 0·12 | — |
| Zn ... | — | — | — | — | — | — | — | — | — | — |
| Pb ... | — | — | — | — | — | — | — | — | 0·26 | 0·08 |
| | 15·99 | 16·06 | 15·89 | 15·78 | 15·99 | 16·27 | 15·87 | 16·06 | (15·10) | 15·85 |
| Bi ... | — | — | — | — | — | — | — | — | 0·09 | — |
| Sb ... | 1·78 | 0·99 | 1·88 | 2·16 | 1·97 | 1·64 | 1·52 | 1·96 | 1·75 | 0·92 |
| As ... | 0·73 | 1·01 | 0·19 | — | 0·17 | 0·32 | 0·35 | 0·15 | 0·23 | 1·13 |
| | (2·51) | 2·00 | 2·07 | 2·16 | 2·14 | 1·96 | 1·87 | 2·11 | 2·07 | 2·05 |
| S ... | (10·50) | 10·94 | 11·04 | 11·06 | 10·87 | 10·77 | 11·26 | 10·83 | (11·83) | 11·10 |
| | 29·00 | 29·00 | 29·00 | 29·00 | 29·00 | 29·00 | 29·00 | 29·00 | 29·00 | 29·00 |

| | 11. | 12. | 13. | 14. | 15. | 16. | 17. | 18. | 19. |
|---|---|---|---|---|---|---|---|---|---|
| Ag ... ... | 62·10 | 64·49 | 64·18 | 64·30 | 64·29 | 62·70 | 57·96 | — | — |
| Cu ... ... | 6·00 | 9·70 | 8·13 | 9·00 | 9·93 | 9·57 | 12·52 | — | — |
| Fe ... ... | 1·10 | 0·41 | — | 0·70 | 0·06 | 0·07 | 0·91 | — | — |
| Zn ... ... | — | 0·34 | — | — | — | — | — | — | — |
| Pb ... ... | — | — | — | — | — | — | — | — | — |
| Bi ... ... | — | — | — | — | — | — | — | — | — |
| Sb ... ... | 9·50 | 8·08 | 11·55 | 4·20 | 5·09 | 10·18 | 5·36 | — | — |
| As ... ... | — | 1·78 | — | 4·10 | 3·74 | 0·78 | 4·60 | — | — |
| S ... ... | 15·30 | 15·10 | 16·14 | 16·10 | 17·04 | (16·70) | 17·45 | — | — |
| | 100·00 | 99·90 | 100·00 | 100·00 | 100·15 | 100·00 | 100·00 | — | — |

11, incl. gangue 6·00. 14, incl. gangue 1·60. 17, incl. gangue 0·67, remainder 0·53.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Ag ... ... | 13·40 | 13·09 | 13·06 | 12·89 | 12·56 | 12·51 | 11·13 | — | — |
| Cu ... ... | 2·20 | 3·34 | 2·81 | 3·06 | 3·29 | 3·24 | 4·08 | — | — |
| Fe ... ... | 0·46 | 0·16 | — | 0·27 | 0·02 | 0·03 | 0·34 | — | — |
| Zn ... ... | — | 0·11 | — | — | — | — | — | — | — |
| Pb ... ... | — | — | — | — | — | — | — | — | — |
| | 16·06 | (16·70) | 15·87 | 16·22 | 15·87 | 15·78 | (15·55) | 15·97 | 16·00 |
| Bi ... ... | — | — | — | — | — | — | — | — | — |
| Sb ... ... | 1·82 | 1·45 | 2·08 | 0·75 | 0·88 | 1·80 | 0·91 | — | — |
| As ... ... | — | 0·52 | — | 1·18 | 1·05 | 0·22 | 1·27 | — | — |
| | 1·82 | 1·97 | 2·08 | 1·93 | 1·93 | 2·02 | 2·18 | 2·02 | 2·00 |
| S ... ... | 11·12 | (10·33) | 11·05 | 10·85 | 11·20 | 11·20 | 11·27 | 11·04 | 11·00 |
| | 29·00 | 29·00 | 29·00 | 29·00 | 29·00 | 29·00 | 29·00 | 29·03 | 29·00 |

1. Keeley mine, South Lorrain, Ontario; new analysis by R. N. Williams; sp.gr. 6·27. 2. Cornwall; anal. Joy (1853, in Hintze, 1904, p. 1174); sp.gr. 6·009. 3. Highland Bell mine, Beaverdell, B.C.; anal. Williams in Staples & Warren (1946); sp.gr. 6·26. 4. Johannesgang, Příbram; anal. Tonner, in Reuss (1860); sp.gr. 6·03. 5. Highland Bell mine, Beaverdell, B.C.; anal. Williams in Staples & Warren (1946); sp.gr. 6·28. 6. 'Arizpe?' Sonora, Mexico; anal. Ungemach (1910). 7. Freiberg,

Saxony; anal. Rose (1833). 8. Santa Lucia mine, Guanajuato, Mexico; anal. Prior (1890); sp.gr. 6·33. 9. Highland Bell mine, Beaverdell, B.C.; anal. Williams in Staples & Warren (1946); sp.gr. 6·33. 10. Quespisiza, Chile; anal. Bodländer (1895). 11. Tres Puntas, Chile; anal. Domeyko (1879). 12. Las Chiapas, Sonora, Mexico; anal. Ungemach (1910). 13. Tres Puntas, Chile; anal. Taylor (1859, in Hintze, 1904, p. 1174). 14. Tres Puntas, Chile; anal. Domeyko (1879). 15. Guarisamez, Durango, Mexico; anal. Rose (1829); sp.gr. 6·214. 16. Terrible lode, Clear Creek County, Colorado; anal. Genth (1886); sp.gr. 6·009. 17. Silver King mine, Yerranderie, New South Wales; anal. White, in Card (1920, in Dana, 1944, p. 352). 18. Average cell content. 19. Ideal cell content, $8(Ag,Cu)_2S.Sb_2S_3$.

duced on pl. II, figs. 1, 2, 3. Owing to the hexagonal pseudo-symmetry several sets of monoclinic lattice planes give identical spacings. In the most general case six different sets of monoclinic planes ($hkl$) are equivalent to one set of hexagonal planes ($hk\bar{i}l$); for example, the sets of planes with the monoclinic symbols (511), (421), (131), ($\bar{1}31$), ($\bar{4}21$), ($\bar{5}11$), all correspond to the set of planes with the hexagonal symbol ($21\bar{3}1$). It is convenient, therefore, to index the powder spectrum with reference to the hexagonal indices. The reversible transformations are: monoclinic to hexagonal, $1\bar{1}0/010/001$; hexagonal to monoclinic, $210/010/001$.

TABLE VI. Polybasite $8(Ag,Cu)_2S.Sb_2S_3$: X-ray powder spectrum.

Monoclinic, $C2/m$; $a = 26{\cdot}12$, $b = 15{\cdot}08$, $c = 23{\cdot}84$ kX, $\beta = 90°\ 00'$; $Z = 16$.
Pseudo-hexagonal, $C$; $a' = 15{\cdot}08$, $c' = 23{\cdot}84$ kX.

| $I.$ | $\theta$ (Cu). | $d$ (meas.). | ($hk\bar{i}l$). | $d$ (calc.). |
|---|---|---|---|---|
| 1 | 12·3° | 3·61 | ($31\bar{4}0$) | 3·622 |
| | | | ($22\bar{4}2$) | 3·594 |
| ½ | 12·8 | 3·47 | ($31\bar{4}2$) | 3·466 |
| ½ | 13·6 | 3·27 | ($40\bar{4}0$) | 3·265 |
| 9 | 14·0 | 3·18 | ($22\bar{4}4$) | 3·186 |
| 10 | 14·9 | 2·99 | ($32\bar{5}0$) | 2·996 |
| | | | (0008) | 2·980 |
| 8 | 15·55 | 2·87 | ($40\bar{4}4$) | 2·864 |
| | | | ($41\bar{5}0$) | 2·850 |
| ½ | 16·15 | 2·76 | ($11\bar{2}8$) | 2·771 |
| 5 | 16·6 | 2·69 | ($31\bar{4}6$) | 2·677 |
| | | | ($32\bar{5}4$) | 2·677 |
| 6 | 17·75 | 2·52 | ($40\bar{4}6$) | 2·523 |
| | | | ($33\bar{6}0$) | 2·513 |
| 4 | 18·55 | 2·42 | ($42\bar{6}2$) | 2·417 |
| 2 | 19·25 | 2·33 | ($22\bar{4}8$) | 2·337 |
| 2 | 20·45 | 2·20 | ($40\bar{4}8$) | 2·201 |
| ½ | 21·00 | 2·14 | ($2.1.\bar{3}.10$) | 2·147 |
| | | | ($43\bar{7}0$) | 2·147 |
| | | | ($60\bar{6}2$) | 2·141 |
| 2 | 21·45 | 2·10 | ($43\bar{7}2$) | 2·113 |
| | | | ($32\bar{5}8$) | 2·113 |
| | | | ($42\bar{6}6$) | 2·097 |
| 1 | 21·95 | 2·06 | ($52\bar{7}2$) | 2·060 |
| | | | ($41\bar{5}8$) | 2·059 |
| 3 | 22·4 | 2·02 | ($51\bar{6}6$) | 2·020 |
| | | | ($43\bar{7}4$) | 2·020 |
| | | | ($2.2.\bar{4}.10$) | 2·015 |
| ½ | 22·95 | 1·971 | ($52\bar{7}4$) | 1·973 |
| | | | ($61\bar{7}2$) | 1·964 |

| $I.$ | $\theta$ (Cu). | $d$ (meas.). | ($hk\bar{i}l$). | $d$ (calc.). |
|---|---|---|---|---|
| 1 | 23·5° | 1·928 | ($4.0.\bar{4}.10$) | 1·925 |
| | | | ($33\bar{6}8$) | 1·921 |
| | | | ($1.1.\bar{2}.12$) | 1·921 |
| | | | ($43\bar{7}6$) | 1·889 |
| 6 | 24·05 | 1·886 | ($61\bar{7}4$) | 1·889 |
| | | | ($44\bar{8}0$) | 1·885 |
| ½ | 24·5 | 1·854 | ($52\bar{7}6$) | 1·851 |
| | | | ($62\bar{8}2$) | 1·791 |
| 1 | 25·5 | 1·785 | ($53\bar{8}4$) | 1·780 |
| | | | ($61\bar{7}6$) | 1·780 |
| | | | ($43\bar{7}8$) | 1·742 |
| 1 | 26·25 | 1·738 | (3.1.$\bar{4}$.12) | 1·742 |
| | | | ($62\bar{8}4$) | 1·733 |
| | | | ($44\bar{8}6$) | 1·703 |
| 3 | 26·85 | 1·702 | (0.0.0.14) | 1·703 |
| | | | (4.0.$\bar{4}$.12) | 1·697 |
| | | | (3.2.$\bar{5}$.12) | 1·656 |
| 2 | 27·7 | 1·654 | ($61\bar{7}8$) | 1·656 |
| | | | ($54\bar{9}2$) | 1·656 |
| 1 | 28·4 | 1·616 | ($80\bar{8}2$) | 1·617 |
| | | | (4.3.$\bar{7}$.10) | 1·595 |
| 2 | 28·9 | 1·590 | ($44\bar{8}8$) | 1·593 |
| | | | ($63\bar{9}4$) | 1·586 |
| | | | ($71\bar{8}6$) | 1·586 |
| | | | (2.2.$\bar{4}$.14) | 1·552 |
| 1 | 29·75 | 1·549 | ($62\bar{8}8$) | 1·548 |
| | | | (4.2.$\bar{6}$.12) | 1·548 |
| | | | (5.1.$\bar{6}$.12) | 1·516 |
| 4 | 30·55 | 1·512 | ($81\bar{9}2$) | 1·516 |
| | | | ($80\bar{8}6$) | 1·510 |
| | | | (4.0.$\bar{4}$.14) | 1·510 |
| 1 | 31·2 | 1·484 | (0.0.0.16) | 1·490 |

TABLE VI. (*cont.*).

| *I.* | θ (Cu). | *d* (meas.). | *I.* | θ (Cu). | *d* (meas.). | *I.* | θ (Cu). | *d* (meas.). |
|---|---|---|---|---|---|---|---|---|
| ½ | 31·8° | 1·459 | ½ | 38·9° | 1·224 | ½ | 41·8° | 1·153 |
| 2 | 32·5 | 1·431 | 1 | 39·5 | 1·208 | 1 | 43·0 | 1·127 |
| 1 | 34·45 | 1·359 | ½ | 40·7 | 1·179 | 1 | 44·8 | 1·091 |
| 1 | 35·05 | 1·338 | ½ | 41·1 | 1·169 | 1 | 46·0 | 1·069 |

PEARCEITE

The two available specimens of pearceite show a dull black mineral with only rough hexagonal tabular form. Specific gravity measurements gave values similar to that noted by Penfield (1896) on analysed material from Montana. Under the microscope thin fragments proved to be practically opaque.

| | sp.gr. | |
|---|---|---|
| Aspen, Colo. (material no. 6) ... ... ... | 6·13 | L. G. Berry |
| Silver, Mont. (material no. 7) ... ... ... | 6·13 | R. M. Thompson |
| Marysville, Mont. ... ... ... ... ... | 6·15 | Penfield (1896) |

*Unit cell.*—The unit cell was determined on both the available specimens by means of rotation and Weissenberg photographs with [001] and [010] or [110] as the rotation axes. Like the photographs of polybasite (pl. II, fig. 6), those of pearceite show hexagonal symmetry as regards the positions of the spots, but only monoclinic symmetry as regards their intensities; but, unlike the polybasite pictures, those of pearceite show no intermediate layer-lines in the rotation photographs about [001] and about [010] or [110] (pl. I), and all the cell dimensions are about one-half of the corresponding dimensions of polybasite, and consequently the cell volume of pearceite is about one-eighth of that of polybasite. The systematically missing spectra of pearceite are those of the space-group $C2/m$.

The measured cell dimensions of pearceite are given below and the resulting axial ratios are compared with the goniometric values of

TABLE VII. Pearceite: Cell dimensions (kX) and axial ratios.

| | *a.* | *b.* | *c.* | *β.* |
|---|---|---|---|---|
| Aspen, Colo. (no. 6) ... ... ... ... | 12·61 | 7·28 | 11·88 | 90° 00′ |
| | 1·732 : | 1 : | 1·631 | |
| Silver, Mont. (no. 7) ... ... ... ... | 12·77 | 7·37 | 11·92 | 90 00 |
| | 1·732 : | 1 : | 1·618 | |
| Marysville, Mont. (Penfield, 1896) ... ... | 1·7309 : | 1 : | 1·6199 | 90 09 |

Penfield (1896). It will be seen that the cell dimensions of the two materials are distinctly different, indicating some substantial difference in their chemical compositions; the structural ratios for Silver, Montana, agree best with Penfield's geometrical ratios.

*Analyses and cell contents.*—The cell content of pearceite was obtained from the cell dimensions and measured specific gravity of the material from Aspen, Colorado, giving the molecular weight $M = 4052$, and combining this number with Penfield's analysis on material from the same locality (table VIII). Although the analysis cannot be regarded as very satisfactory the empirical cell content gives very nearly:

$$Ag_{22}Cu_{10}As_4S_{22} = 2[8(Ag,Cu)_2S.As_2S_3]$$

which yields the calculated specific gravity 6·07.

TABLE VIII. Pearceite from Aspen, Colorado: Analysis and cell content. $M = 4052$.

| | | 1. | 2. | | 3. |
|---|---|---|---|---|---|
| Ag | ... ... | 56·90 | 22·30 | 32·18 | 32 |
| Cu | ... ... | 14·85 | 9·88 | | |
| Sb | ... ... | 0·30 | 0·10 | 4·06 | 4 |
| As | ... ... | 7·01 | 3·96 | | |
| S | ... ... | 16·75 | 22·10 | 22·10 | 22 |
| | | 95·81 | | 58·34 | 58 |

1. Mollie Gibson mine, Aspen, Colorado; anal. Penfield, in Penfield & Pearce (1892). After calculation to 100 per cent. after withdrawing 12·81 per cent. of impurities, and removal of Zn 2·81, S 1·38 for blende. 2. Empirical cell content. 3. Ideal cell content.

In table IX all the available analyses of pearceite are expressed in terms of a sum of 29 atoms or half the content of the unit cell. It will be seen that Cu replaces Ag from about 1/16 to 1/3 of the total (Ag,Cu) component; on the other hand, only trivial amounts of Sb take the

TABLE IX. Pearceite: Analyses and cell contents.

| | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. |
|---|---|---|---|---|---|---|---|---|
| Ag ... | 72·43 | 63·54 | 59·73 | 56·90 | 59·22 | 55·17 | — | — |
| Cu ... | 3·04 | 10·70 | 12·91 | 14·85 | 15·65 | 18·11 | — | — |
| Fe ... | 0·33 | 0·60 | — | — | — | 1·05 | — | — |
| Zn ... | 0·59 | — | — | — | — | — | — | — |
| Sb ... | 0·25 | 0·43 | 0·18 | 0·30 | — | — | — | — |
| As ... | 6·23 | 7·29 | 6·29 | 7·01 | 7·56 | 7·39 | — | — |
| S ... | 16·83 | 17·07 | 16·18 | 16·75 | 17·46 | 17·71 | — | — |
| | 99·70 | 99·63 | 95·29 | 95·81 | 99·89 | 99·85 | — | — |
| | | | 6, including insol. 0·42. | | | | | |
| Ag ... | 14·48 | 12·20 | 11·92 | 11·09 | 11·05 | 10·12 | — | — |
| Cu ... | 1·03 | 3·48 | 4·37 | 4·91 | 4·96 | 5·63 | — | — |
| Fe ... | 0·12 | 0·22 | — | — | — | 0·37 | — | — |
| Zn ... | 0·24 | — | — | — | — | — | — | — |
| | 15·87 | 15·90 | 16·29 | 16·00 | 16·01 | 16·12 | 16·03 | 16·00 |

TABLE IX (*cont.*).

| | | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. |
|---|---|---|---|---|---|---|---|---|---|
| Sb | ... | 0·04 | 0·07 | 0·03 | 0·05 | — | — | — | — |
| As | ... | 1·79 | 2·01 | 1·82 | 1·97 | 2·03 | 1·96 | — | — |
| | | 1·83 | 2·08 | 1·85 | 2·02 | 2·03 | 1·96 | 1·96 | 2·00 |
| S | ... | 11·30 | 11·02 | 10·86 | 10·98 | 10·96 | 10·92 | 11·00 | 11·00 |
| | | 29·00 | 29·00 | 29·00 | 29·00 | 29·00 | 29·00 | 28·99 | 29·00 |

1. Schemnitz, Hungary; anal. Rose (1833). 2. Arqueros, Chile; anal. Domeyko (1879, p. 393); sp.gr. 6·33. 3. Mollie Gibson mine, Aspen, Colorado; anal. Pearce in Penfield & Pearce (1892); recalculated after deduction of 28·18 per cent. of impurities and 4·71 per cent. of ZnS; sp.gr. 6·03. 4. Mollie Gibson mine, Aspen, Colorado; anal. Penfield in Penfield & Pearce (1892); recalculated after deduction of 12·81 per cent. of impurities and 4·19 per cent. of ZnS; sp.gr. 6·080. 5. Veta Rica mine, Sierra Mojada, Mexico; anal. Dubois in Van Horn & Cook (1911); sp.gr. 6·062. 6. Drumlummon mine, Marysville, Montana; anal. Knight in Penfield (1896). 7. Average cell content. 8. Ideal cell content for $8(Ag,Cu)_2S.As_2S_3$.

place of As. Since considerable substitution of Cu for Ag appears to have little effect on the cell dimensions of polybasite it is difficult to explain the considerable variation found in pearceite. Possibly Zn and Fe actually enter the structure in some cases, as suggested by the early analysis of Rose.

*X-ray powder patterns.*—The two specimens of pearceite gave X-ray powder patterns (pl. II, figs. 4, 5) which differ slightly, in keeping with their slightly different cell dimensions, and show distinct differences when compared to the pattern of polybasite (pl. II, figs. 1, 2, 3). The two pearceite patterns have therefore been indexed separately, with reference to hexagonal elements.

TABLE X. Pearceite, $8(Ag,Cu)_2S.As_2S_3$; Aspen, Colorado.
X-ray powder spectrum.

Monoclinic, $C2/m$; $a = 12{\cdot}61$, $b = 7{\cdot}28$, $c = 11{\cdot}88$ kX, $\beta = 90°\ 00'$; $Z = 2$.
Pseudo-hexagonal, $C$; $a' = 7{\cdot}28$, $c' = 11{\cdot}88$ kX.

| *I.* | $\theta$ (Cu). | *d* (meas.). | (*hkil*). | *d* (calc.). | *I.* | $\theta$ (Cu). | *d* (meas.). | (*hkil*). | *d* (calc.). |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 14·35° | 3·10 | $(11\bar{2}2)$ | 3·104 | 1 | 23·95° | 1·893 | $(20\bar{2}5)$ | 1·897 |
| 2 | 14·65 | 3·04 | $(20\bar{2}1)$ | 3·047 | | | | $(10\bar{1}6)$ | 1·889 |
| 10 | 15·05 | 2·96 | (0004) | 2·970 | 2 | 24·5 | 1·854 | $(21\bar{3}4)$ | 1·859 |
| 9 | 16·0 | 2·79 | $(20\bar{2}2)$ | 2·785 | | | | $(30\bar{3}3)$ | 1·856 |
| 6 | 18·15 | 2·47 | $(20\bar{2}3)$ | 2·466 | 6 | 24·95 | 1·823 | $(22\bar{4}0)$ | 1·820 |
| 5 | 19·2 | 2·34 | $(21\bar{3}1)$ | 2·337 | ½ | 25·3 | 1·799 | $(22\bar{4}1)$ | 1·799 |
| 6 | 19·55 | 2·30 | $(11\bar{2}2)$ | 2·301 | 3 | 27·35 | 1·673 | $(20\bar{2}6)$ | 1·677 |
| ½ | 20·3 | 2·22 | $(10\bar{1}5)$ | 2·223 | | | | $(31\bar{4}2)$ | 1·677 |
| | | | $(21\bar{3}2)$ | 2·212 | ½ | 27·75 | 1·651 | $(22\bar{4}3)$ | 1·654 |
| 3 | 20·85 | 2·16 | $(20\bar{2}4)$ | 2·162 | 1 | 29·6 | 1·556 | $(22\bar{4}4)$ | 1·552 |
| ½ | 21·45 | 2·10 | $(30\bar{3}0)$ | 2·102 | 1 | 30·35 | 1·521 | $(40\bar{4}2)$ | 1·523 |
| 1 | 21·8 | 2·07 | $(30\bar{3}1)$ | 2·070 | | | | $(21\bar{3}6)$ | 1·523 |
| 2 | 22·15 | 2·04 | $(21\bar{3}3)$ | 2·042 | 2 | 31·05 | 1·490 | $(20\bar{2}7)$ | 1·494 |
| 5 | 22·75 | 1·988 | $(11\bar{2}5)$ | 1·990 | | | | (0008) | 1·485 |
| | | | $(30\bar{3}2)$ | 1·981 | | | | | |

TABLE X (*cont.*).

| *I.* | θ (Cu). | *d* (meas.). | *I.* | θ (Cu). | *d* (meas.). | *I.* | θ (Cu). | *d* (meas). |
|---|---|---|---|---|---|---|---|---|
| 1 | 31·7° | 1·463 | ½ | 37·1° | 1·274 | ½ | 42·45° | 1·139 |
| 1 | 32·5 | 1·444 | 1 | 38·55 | 1·233 | ½ | 42·95 | 1·128 |
| 1 | 33·5 | 1·393 | 1 | 39·2 | 1·216 | 1 | 45·35 | 1·080 |
| ½ | 34·2 | 1·368 | 1 | 40·25 | 1·190 | ½ | 46·15 | 1·066 |
| 1 | 34·85 | 1·345 | 1 | 41·15 | 1·168 | ½ | 46·95 | 1·052 |
| ½ | 35·7 | 1·324 | 1 | 41·65 | 1·157 | ½ | 48·85 | 1·021 |

TABLE XI. Pearceite, $8(Ag,Cu)_2S.As_2S_3$; Silver, Montana. X-ray powder spectrum.

Monoclinic, $C2/m$; $a = 12{\cdot}77$, $b = 7{\cdot}37$, $c = 11{\cdot}92$ kX, $\beta = 90°\ 00'$; $Z = 2$.
Pseudo-hexagonal, $C$; $a' = 7{\cdot}37$, $c' = 11{\cdot}92$ kX.

| *I.* | θ (Cu). | *d* (meas.). | (*hkil*). | *d* (calc.). | *I.* | θ (Cu). | *d* (meas.). | (*hkil*). | *d* (calc.). |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 6·8° | 6·5 | $(10\bar{1}0)$ | 6·385 | 4 | 22·5° | 2·01 | $(30\bar{3}2)$ | 2·004 |
| 1 | 7·3 | 6·0 | (0002) | 5·960 | | | | $(11\bar{2}5)$ | 2·002 |
| 1 | 11·95 | 3·71 | $(11\bar{2}0)$ | 3·685 | 1 | 23·75 | 1·908 | $(20\bar{2}5)$ | 1·910 |
| ½ | 12·5 | 3·55 | $(11\bar{2}1)$ | 3·522 | | | | $(10\bar{1}6)$ | 1·897 |
| 5 | 14·35 | 3·10 | $(11\bar{2}2)$ | 3·135 | ½ | 24·15 | 1·879 | $(30\bar{3}3)$ | 1·876 |
| | | | $(20\bar{2}1)$ | 3·084 | | | | $(21\bar{3}4)$ | 1·875 |
| 10 | 14·9 | 2·99 | (0004) | 2·980 | 5 | 24·6 | 1·846 | $(22\bar{4}0)$ | 1·842 |
| 9 | 15·75 | 2·83 | $(20\bar{2}2)$ | 2·814 | ½ | 25·0 | 1·819 | $(22\bar{4}1)$ | 1·821 |
| 4 | 17·95 | 2·49 | $(20\bar{2}3)$ | 2·489 | | | | $(31\bar{4}2)$ | 1·697 |
| 3 | 18·95 | 2·37 | $(21\bar{3}1)$ | 2·365 | 3 | 27·0 | 1·693 | $(21\bar{3}5)$ | 1·696 |
| 5 | 19·35 | 2·32 | $(11\bar{2}2)$ | 2·317 | | | | $(20\bar{2}6)$ | 1·687 |
| ½ | 20·1 | 2·24 | $(21\bar{3}2)$ | 2·237 | ½ | 27·35 | 1·673 | $(22\bar{4}3)$ | 1·672 |
| | | | $(10\bar{1}5)$ | 2·233 | ½ | 29·4 | 1·566 | $(22\bar{4}4)$ | 1·567 |
| 3 | 20·65 | 2·18 | $(20\bar{2}4)$ | 2·178 | ½ | 29·9 | 1·542 | $(11\bar{2}7)$ | 1·545 |
| ½ | 21·0 | 2·14 | $(30\bar{3}0)$ | 2·128 | | | | $(40\bar{4}2)$ | 1·542 |
| 2 | 21·55 | 2·09 | $(30\bar{3}1)$ | 2·095 | 1 | 30·7 | 1·506 | $(20\bar{2}7)$ | 1·502 |
| 2 | 21·85 | 2·06 | $(21\bar{3}3)$ | 2·062 | 1 | 31·1 | 1·488 | (0008) | 1·490 |

| *I.* | θ (Cu). | *d* (meas.). | *I.* | θ (Cu). | *d* (meas.). |
|---|---|---|---|---|---|
| 1 | 31·8° | 1·459 | 1 | 34·6° | 1·354 |
| 1 | 33·15 | 1·406 | 1 | 38·0 | 1·248 |

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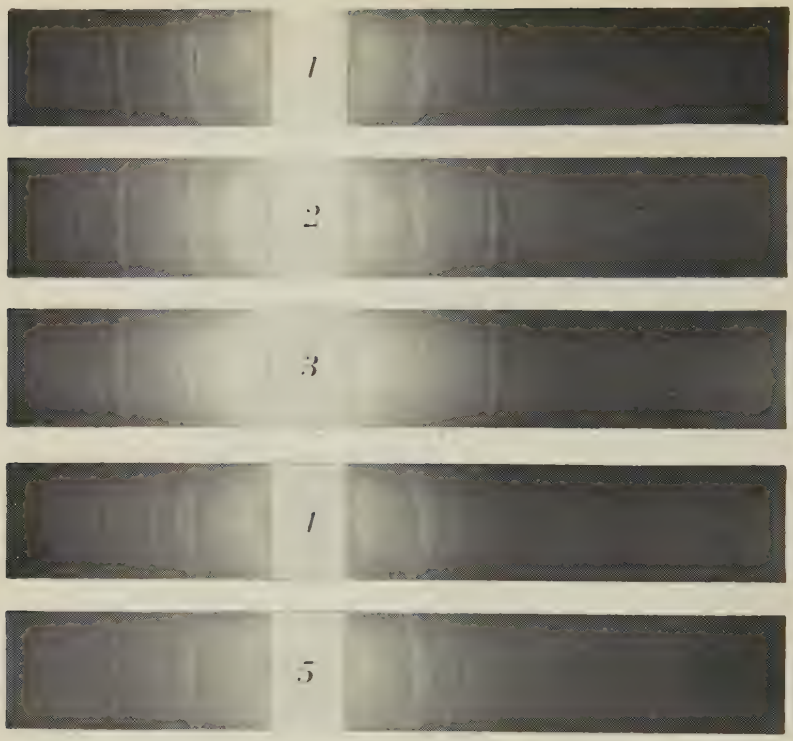

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## Explanation of Plates I and II.

X-ray photographs of polybasite and pearceite.

Plate I.—X-ray single-crystal photographs with Cu radiation; camera radius $90/\pi$ mm. ($1^\circ\ \theta = 1$ mm. on film); full-size reproductions of contact prints.

Fig. 1. Polybasite, Las Chiapas mine, Sonora, Mexico; rotation about [010], giving $b = 15{\cdot}08$ kX.

Fig. 2. Pearceite, Aspen, Colorado; rotation about [010], giving $b = 7{\cdot}28$ kX.

Plate II.—Figs. 1 5, X-ray powder photographs with Cu radiation, Ni filter; camera radius $90/\pi$ mm. ($1^\circ\ \theta = 1$ mm. on film); full-size reproductions of contact prints.

Fig. 1. Polybasite, Highland Bell mine, Beaverdell, B.C.

Fig. 2. Polybasite, Keeley mine, South Lorrain, Ontario.

Fig. 3. Polybasite, Las Chiapas mine, Sonora, Mexico.

Fig. 4. Pearceite, Aspen, Colorado.

Fig. 5. Pearceite, Silver, Montana.

Fig. 6. X-ray single-crystal photograph, as on plate I. Polybasite, Keeley mine, South Lorrain, Ontario. Weissenberg resolution of the layer ($h0l$) or ($hhl$), showing lack of symmetry of intensity about the ($00l$) row (most prominent slanting row), and therefore the lack of an even-fold vertical symmetry-axis.

# *Extinction in X-ray crystallography.*

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## *Historical introduction.*

EXTINCTION is the increase in absorption that is to be expected when Bragg reflection of X-rays takes place in single crystals, and the corresponding decrease in intensity of reflection observed.

The increase of absorption was directly observed in 1914 in two ways. Using the ionization spectrometer, W. H. Bragg[1] found that the amount of radiation transmitted by a crystal section was notably decreased when the transmitted beam had suffered reflection from a set of crystal planes. A photographic method was used by Rutherford and Andrade,[2] who allowed a divergent beam of $\gamma$-rays to traverse a rocksalt crystal and who observed a pattern of absorption lines on a photographic plate so placed as to receive the transmitted radiation. Neither of these methods was developed to give quantitative measurements owing to the difficulty of making allowance for the divergency and inhomogeneity of the radiation, and the imperfections of the crystal.

Early observations on the intensity of X-ray reflection were much more informative, although at first very puzzling. Ionization spectrometer methods were used, reflections being observed from the surface or through the thickness of large single-crystal plates, which were chosen to be as perfect as possible. Darwin[3] had calculated in 1914 the intensity and angular width of the reflection to be expected from a perfect crystal, and in 1918, independently and by a different method, Ewald[4] obtained similar results. Comparison with experiment showed that the actual intensities observed were always *greater* than those expected from the calculation, however carefully the crystal specimens might be selected. Further experiment showed that the Bragg reflection from a crystal surface could be *increased* to a considerable extent by

[1] W. H. Bragg, Nature, London, 1914, vol. 43, p. 31.
[2] E. Rutherford and E. N. da C. Andrade, Phil. Mag., 1914, ser. 6, vol. 28, p. 263.
[3] C. G. Darwin, Phil. Mag., 1914, ser. 6, vol. 27, p. 675.
[4] P. P. Ewald, Ann. Physik, 1918, vol. 54, p. 519.

grinding or polishing the surface, a process which undoubtedly produced a fairly deep layer of somewhat disorientated crystallites. It seemed at first surprising that the X-ray reflection from a mosaic of partly disalined crystallites should be many times more intense than that from a much more perfect crystal, but this observation was in complete agreement with later theoretical findings, for Darwin showed that the reflection from a 'perfectly imperfect' or completely mosaic crystal would, in fact, be up to forty or more times as intense as that from an 'ideal' or perfectly monolithic crystal.[1] Observed values were found to fall between the two extremes, but were usually much nearer to the 'mosaic' value.[2] From an X-ray point of view, most crystals are comparatively imperfect.

To the earlier workers, this influence of crystal *texture* was not only difficult to understand fully, but was also definitely an obstacle to be overcome, before the more interesting questions of atomic arrangement and scattering power could be effectively investigated. We are now getting to the stage, however, where the question of crystal texture is of interest in itself, and extinction is once again receiving consideration, but from quite another angle.

*The nature of the problem.*

What does, in fact, happen to a beam of parallel, monochromatic X-rays when it is incident on the face of a crystal? That depends on the wave-length of the rays, the nature, texture, and structure of the crystal, and the angle of incidence. If the angle of grazing incidence is sufficiently small, total reflection will take place from either crystalline or non-crystalline solids. The critical angle is given by the formula $\frac{1}{2}\theta_c^2 = 1{\cdot}35.10^{10}.\rho\lambda_0^2$ where $\theta_c$ is expressed in radians, $\rho$ is density in gr./c.c., and $\lambda_0$ the incident wave-length in cm. Hence for soda-glass and Cu$K\alpha$ radiation $\theta_c = 14'$; for steel and Cr$K\alpha$, $\theta_c = 38'$. For angles of incidence greater than $\theta_c$ the rays will enter the crystal and will be bent away from the normal in doing so. The refractive index $\mu$ is only a little less than unity, the amount of defect $(1 - \mu)$ being given by $1{\cdot}35.10^{10}.\rho\lambda_0^2$, provided that $\lambda_0$ is not near to any of the characteristic wave-lengths of atoms in the crystal (or more strictly, provided that the frequency of the incident waves is not near to any of the resonance frequencies of the component atoms). $(1 - \mu)$ is therefore of the order of

[1] C. G. Darwin, Phil. Mag., 1922, ser. 6, vol. 43, p. 800.
[2] W. L. Bragg, C. G. Darwin, and R. W. James, Phil. Mag., 1926, ser. 7, vol. 1, p. 897; R. W. James, Zeits. Krist., 1934, vol. 89, p. 295.

$10^{-5}$ or $10^{-6}$, and may be neglected except in precision work, where it has chiefly to be considered in the case of dense crystals and long wave-lengths.

The X-rays on entering the crystal lose energy, partly by transformation, partly by scattering. Some energy may be used in ionizing atoms, with the production of $\beta$ rays, and this energy may reappear as fluorescent X-radiation of longer wave-lengths than that producing it. Some energy is used up in giving momentum to free or freed electrons and this is accompanied by the emission of scattered radiation also of longer wave-lengths (Compton effect), incoherent with the primary radiation. Some energy reappears as heat, due to increased vibration of atoms or molecules. X-rays are also scattered by the outer electrons of the atoms; since the atoms are always vibrating about their mean positions or may even be displaced permanently from the regular lattice points; and since in any case the electron clouds are extended, and not concentrated at the exact lattice points, a good deal of this scattered radiation is incoherent or only approximately coherent, and it forms a general background of diffuse, uneven but weak scattering which cannot be altogether avoided however the crystal is orientated. The fact that the atoms in a crystal are, on the whole, regularly arranged, however, means that *under certain conditions* the scattered radiation from these atoms will be coherent and will interfere constructively to give discrete diffracted (selectively reflected) beams. The total angle of diffraction within the crystal, $2\theta$, is given by the Bragg relation $n\lambda = 2d \sin \theta$, where $d$ is the spacing of the set of crystal planes on which the primary beam is incident in the crystal at angle $\theta$, and $\lambda$ is the wave-length in the crystal. The main transmitted beam, which corresponds to $n = 0$, is reduced both by this selective reflection and by ordinary absorption, the latter term being understood to include all the other effects described above: conversion into $\beta$-rays or fluorescent X-radiation, Compton effect, heating, and incoherent scattering effects.

The ordinary absorption is, relatively speaking, easy to deal with. Except in the neighbourhood of an absorption edge, it is comparatively straightforward to measure. It *must*, however, be measured under conditions where coherent constructive interference cannot take place. *This means that a single crystal must be used and the orientation must be such that the Bragg relation is not satisfied or even nearly satisfied for any set of planes.*

Let us suppose, however, that the absorption is measured, using a single crystal, in a direction corresponding to which some selective

reflection *is* taking place. Clearly the absorption will appear to be much greater than its normal value, because the transmitted beam will have been reduced not only by conversion into $\beta$ rays, &c., but also by the redirection of energy into the reflected beam. By how much the absorption is increased depends principally upon the *texture* of the crystal. If the crystal is perfect the absorption along those directions in which selective reflection takes place may be thirty or even a hundred times as large as the ordinary value. It is so large that the transmitted beam does not penetrate far into the crystal, whose lower layers, therefore, do not get a chance to scatter or to reflect the X-rays at all. This enormously enhanced absorption in a single crystal which has an extended perfect arrangement of atoms is called *primary extinction.* Now, why should primary extinction diminish the *reflected* beam, as it certainly does? In non-mathematical language, the reason is this: A perfect crystal reflects X-rays almost perfectly over a *very limited range* of angle on each side ($\theta \pm s$) of the Bragg angle $\theta$, where $s = q\lambda/2\pi d \cos\theta$ ($q$ = fraction of the incident amplitude reflected from a single plane) and is of the order of a few seconds of arc. [In practice this formula must be modified to allow for the finite width of an X-ray line, for the fact that the crystal is finite and for differences in the diffraction curves for the two polarized components of the reflected beam.] The rays suffer a change of phase of $\pi/2$ on reflection, and therefore of $\pi$ on double reflection. A doubly reflected ray travels in the same direction as the incident ray, but tends to interfere with it destructively because of its opposite phase. A triply reflected ray travels in the same direction as the once-reflected ray but is again of opposite phase and therefore tends to reduce its intensity. The transmitted beam therefore loses energy both by the reflection of energy away in other directions and by the existence of scattered radiation parallel in direction but opposite in phase to itself. The reflected beam loses energy also through multiple reflection which redirects energy away from its own direction, or into its own direction with opposite phase. It is only in a perfectly regular crystal that these phase relationships, which together with the ordinary absorption result eventually in a complete annihilation (or extinction) of the transmitted beam, can exist. But this is not all. The lower parts of the crystal are not reached by X-rays at the correct angle for reflection and do not therefore make any contribution to the reflected beam. The enhanced absorption effectively limits the reflecting power of the crystal to a 'skin', whose depth depends on the angle and intensity of reflection, but which is of the order of some $10^{-4}$ cm. If the crystallites

in a mosaic or powder are of smaller dimensions than this, then primary extinction is unimportant because the whole of the crystallite will be reflecting; in a sense, it will all be 'skin'. But if the thickness over which the crystal arrangement is perfect is larger than this, then some of the crystal will be quite ineffective for reflection purposes.

Darwin has shown that the ordinary formula for the intensity of reflection from the face of a crystal can be modified to allow for primary extinction by the introduction of a factor[1] tanh $\mathbf{m}q/\mathbf{m}q$ where $\mathbf{m}$ = number of perfect planes occurring in regular succession and $q$ is defined as before. The expression is not strictly applicable unless $\mathbf{m}q$ is small, and a somewhat different expression is necessary for other conditions of reflection, for example, through a thin plate,[2] but it will give an indication of the correction to be applied. The expression is almost *independent of wave-length*, because $q = 2Ne^2.d^2F(hkl)/mc^2$ (neglecting the polarization factor), where $N$ is the number of pattern units/unit volume, $d$ the spacing, $F(hkl)$ the structure factor, and $e$, $m$, $c$ have their usual meanings. Table I gives the value of the expression for the first five orders of reflection from the cleavage face of rocksalt crystals of various thickness.

TABLE I.

| | | $d$ | | $\mathbf{m}$ *for* $D$(cm.) | | | (tanh $\mathbf{m}q$)/$\mathbf{m}q$ | | |
|---|---|---|---|---|---|---|---|---|---|
| *n.* | *hkl.* | (Å.U.) | $q$. | $D = 10^{-3}$. | $10^{-4}$. | $10^{-5}$. | $D = 10^{-3}$. | $10^{-4}$. | $10^{-5}$. |
| 1 | 200 | 2·814 | $2{\cdot}05\times10^{-4}$ | $3{\cdot}55\times10^{4}$ | $\times10^{3}$ | $\times10^{2}$ | 0·14 | 0·85 | 1·00 |
| 2 | 400 | 1·407 | $0{\cdot}30_7$ „ | 7·10 „ | „ | „ | 0·46 | 0·98 | 1·00 |
| 3 | 600 | 0·938 | $0{\cdot}08_1$ „ | 10·65 „ | „ | „ | 0·81 | 1·00 | 1·00 |
| 4 | 800 | 0·703 | $0{\cdot}02_6$ „ | 14·20 „ | „ | „ | 0·90 | 1·00 | 1·00 |
| 5 | 10.0.0 | 0·563 | $0{\cdot}00_9$ „ | 17·75 „ | „ | „ | 0·99 | 1·00 | 1·00 |

Table II gives the primary extinction factor for the first five observable reflections from a diamond plate.

TABLE II.

| | | $\mathbf{m}$ *for* | | (tanh $\mathbf{m}q$)/$\mathbf{m}q$ | |
|---|---|---|---|---|---|
| *hkl.* | $q$. | $D = 10^{-3}$. | $10^{-4}$ cm. | $D = 10^{-3}$. | $10^{-4}$ cm. |
| 111 | $9{\cdot}84\times10^{-5}$ | $4{\cdot}87\times10^{4}$ | $\times10^{3}$ | 0·21 | 0·93 |
| 220 | 2·85 „ | 7·95 „ | „ | 0·45 | $0{\cdot}98_2$ |
| 113 | 1·22 „ | 9·32 „ | „ | 0·71 | $0{\cdot}99_5$ |
| 004 | 1·09 „ | 11·24 „ | „ | 0·68 | $0{\cdot}99_4$ |
| 331 | 0·65 „ | 12·25 „ | „ | 0·83 | $0{\cdot}99_8$ |

An alternative and rather useful form of the expression tanh $\mathbf{m}q/\mathbf{m}q$ is $(1-\mathbf{m}^2q^2/3+2\mathbf{m}^4q^4/15-17\mathbf{m}^6q^6/315+\ldots)$ which shows the sharp

[1] Hyperbolic tangent, tanh $x = (e^x-e^{-x})/(e^x+e^{-x})$.
[2] I. Waller, Ann. Physik, 1926, vol. 79, p. 261.

dependence of the extinction factor upon both **m** and $q$. It is clear, however, from the examples given that the *primary extinction* factor is only of importance when the thickness $D$ of perfectly regular atomic arrangement is greater than about $10^{-4}$ cm. and *chiefly affects intensely reflecting planes* ($q$ large) *especially when these are of small spacing* (**m** large). In order to be sure that primary extinction is eliminated, it is usual to powder the specimen so finely that the maximum particle size is less than, say, $0{\cdot}5 \times 10^{-4}$ cm., or, in the case of reflection from a crystal face, to grind the face with a fine abrasive. Immersion in liquid air will also greatly diminish the primary extinction in a single crystal in some cases, although it may not remove it altogether, because the crystal tends to break up on a large scale as well as on a small one, and to disintegrate before the small-scale breaking up is complete.

Irregularities of atomic arrangement in crystals may take different forms. The crystal planes may be warped or distorted, or the spacings may not be quite uniform. The crystal may be composed of a mosaic of tiny perfect crystallites, nearly but not quite parallel to each other; or the crystallites may be parallel but separated by discontinuities at the inter-surfaces. In all these cases, and especially the last, multiple reflection may occur, but the phase relationships which led to destructive interference for both transmitted and reflected beams in the case of a large perfect crystal can no longer exist, because the continuity of arrangement has gone. In all such cases, however, the ordinary linear absorption will be increased in directions corresponding to which there is selective reflection. Energy $Q$ having been removed from the incident beam to form the reflected beam, the amount left to be transmitted will be smaller than if such selective reflection had not taken place. The factor by which $\mu$ is increased on account of selective reflection $Q$ is $gQ$, where $g$ is a constant of the crystal and is independent of the wavelength $\lambda$.[1] If multiple reflection occurs so that energy is redirected into the direction of the transmitted beam (though not now with any phase relationship), then an expression of the form $\mu' = \mu + gQ - g'Q^2 + \ldots$ may be necessary, where $g'Q^2$ and higher terms depend not only on the texture of the crystal but also on other experimental factors. This increase of absorption due to selective reflection is known as *secondary extinction*, and it leads to a decrease of the intensity of reflection, because although the transmitted beam does reach the lower layers of the crystal, yet it is not so strong as if no selective reflection had already

[1] R. W. James and E. M. Frith, Proc. Roy. Soc. London, Ser. A, 1927, vol. 117, p. 62.

occurred in the upper layers. The proportion, $\rho$, of the energy of the incident beam which is reflected away in a given time is, in fact, inversely dependent upon the absorption coefficient $\mu$, and if $\mu$ is increased to $\mu'$, $\rho$ will be decreased. For reflection from a crystal face of a deep crystal, $\rho = Q/2\mu'$ where $Q$ is not the theoretical intensity of reflection, but is the actual intensity (i.e. the theoretical value corrected for primary extinction; $(Q_0 \tanh \mathbf{m}q)/\mathbf{m}q$ in this case). For reflection through a crystal plate, thickness $t_0$, $\rho = Qt.e^{-\mu' t}$ where $t = t_0 \sec\theta$; and the *maximum* value of $\rho$ will be found for a plate in which the length of path $t = 1/\mu'$, so that $\rho_{\max.} = Q/e\mu'$ (always less, therefore, than the reflection from a face, $Q/2\mu'$). $\mu'$ may be measured directly for any given reflection and wave-length by plotting $\rho$ against $t_0 = t/\sec\theta$; $\mu'$ corresponds to the value of $t_0$ for which the curve has its maximum and for which, therefore, $1/(t_0 \sec\theta) = \mu' = \mu + gQ - g'Q^2 \ldots$. In order to find $g$, $g'$, &c., this procedure would have to be carried out for more than one set of crystal planes. Using this method for a particular NaCl crystal, Bragg, James, and Bosanquet[1] found $g = 320$, $g'$, &c., negligible.

*Comparison of primary and secondary extinction factors.*

Writing $\rho = Q/2\mu'$ and $\rho = Qt.e^{-\mu' t}$ in the forms $(Q/2\mu).\mu/(\mu+gQ)$ and $(Qt.e^{-\mu t})e^{-gQt}$, it is possible to compare the effect of secondary extinction in the two different sets of experimental conditions and also to see how the secondary compares with the primary extinction factor for reflection from a face. Neglecting polarization, as before, $Q_0$ may be expressed as $\frac{1}{2}(q^2\lambda \tan\theta)$ and therefore, although $q$ is almost independent of $\lambda$, $Q_0$ is not. This introduces an important difference between the two kinds of extinction: *secondary extinction varies with wave-length; primary extinction is almost independent of it.* For a given wave-length, crystal texture and experimental method will decide which is the more important. A second important distinction is that while *primary extinction depends only on perfect crystallite size, secondary extinction depends not only on perfect crystallite size, but also, in the case of transmission, on the over-all size of the crystal.* The dependence on perfect crystallite size occurs because if primary extinction exists, it will powerfully affect the value of the secondary extinction through its influence on $Q$. For a perfect single crystal of linear dimensions, say, $0{\cdot}5 \times 10^{-4}$ cm. or less, primary extinction is negligible, and it is equally negligible for a single mosaic crystal composed of crystallites of this size. For a perfect crystal

[1] W. L. Bragg, R. W. James, and C. H. Bosanquet, Phil. Mag., 1921, ser. 6, vol. 42, p. 1.

(or a conglomerate of perfect crystallites) $10^{-3}$ cm. in size, primary extinction is already very important and for a perfect crystal $10^{-2}$ cm. or larger, the expression $(\tanh \mathbf{m}q)/\mathbf{m}q$ is no longer a sufficiently good approximation to be used, and it is better to use Darwin's original formula for the intensity of reflection from a perfect crystal.

For a perfect single crystal of linear dimensions $10^{-4}$ or even $10^{-3}$ cm., secondary extinction is negligible, but it is *not* negligible for a larger mosaic crystal composed of crystallites of this size, though it will be more important for the conglomerate of smaller than for that of larger crystallites.

Table III shows the relative effect of secondary extinction in the case of (*a*) transmission, (*b*) reflection, from a crystal face, for NaCl crystals 0·1 and 0·01 cm. thickness which are composed of crystallites, say, $10^{-5}$ cm. diameter, so that primary extinction is negligible.

TABLE III.

| | Cu$K\alpha$. | | | Mo$K\alpha$. | | |
|---|---|---|---|---|---|---|
| *hkl.* | $e^{-gQ0\cdot1}$. | $e^{-gQ0\cdot01}$. | $\frac{\mu}{\mu+gQ}$. | $e^{-gQ0\cdot1}$. | $e^{-gQ0\cdot01}$. | $\frac{\mu}{\mu+gQ}$. |
| 200 | 0·05 | 0·74 | 0·84 | 0·51 | 0·93 | 0·71 |
| 400 | 0·64 | 0·96 | 0·97 | 0·88 | 0·99 | 0·93 |
| 600 | 0·86 | 0·99 | 0·99 | 0·98 | 1·00 | 0·99 |
| 800 | ..... not observable | | | 1·00 | 1·00 | 1·00 |
| 10.0.0 | ..... | | | 1·00 | 1·00 | 1·00 |

It is not, strictly speaking, correct to take the same value of $g$ (320) for the two experimental methods, but the results will at least show the trend of the correction. In practice, $g$ should be determined for the crystal and conditions used, but this is by no means easy.[1]

Table IV shows the relative effect of primary and secondary extinction for reflection from the face of a NaCl crystal composed of crystallites (*a*) $10^{-3}$, (*b*) $10^{-4}$ cm. diameter, for the same two radiations.

TABLE IV.

| | Primary $\left(\frac{\tanh \mathbf{m}q}{\mathbf{m}q}\right)$. | | Secondary $\left(\frac{\mu}{\mu+gQ_0\frac{\tanh \mathbf{m}q}{\mathbf{m}q}}\right)$. | | | |
|---|---|---|---|---|---|---|
| | Cu$K\alpha$ or Mo$K\alpha$. | | Cu$K\alpha$. | | Mo$K\alpha$. | |
| *hkl.* | $D = 10^{-3}$. | $10^{-4}$ cm. | $10^{-3}$. | $10^{-4}$. | $10^{-3}$. | $10^{-4}$ cm. |
| 200 | 0·14 | 0·85 | 0·97 | 0·86 | $0\cdot94_5$ | 0·74 |
| 400 | 0·46 | 0·98 | 0·99 | 0·97 | 0·97 | 0·93 |
| 600 | 0·81 | 1·00 | 0·99 | 0·99 | 0·99 | 0·99 |
| 800 | 0·90 | 1·00 | — | — | 1·00 | 1·00 |
| 10.0.0 | 0·99 | 1·00 | — | — | 1·00 | 1·00 |

[1] W. L. Bragg, R. W. James, and C. H. Bosanquet, Phil. Mag., 1921, ser. 6, vol. 42, p. 1.

*Primary and secondary extinction in powders.*

Primary extinction is negligible if the crystallites in a powdered specimen are less than about $0{\cdot}5 \times 10^{-4}$ cm. diameter. Secondary extinction is never negligible on transmission through a thick specimen composed of fine crystallites, although it will be reduced to a minimum by giving the crystallites a random orientation. As long as energy is deflected from the transmitted beam by selective reflection, secondary extinction must exist. Whether the powder is used in the form of a cylinder, a briquette, foil, or sheet, selective reflection will always take place, and the absorption measured in a certain thickness of such a powder will always (allowance being made for difference of density due to faulty packing) be greater than that measured in an equal thickness of single crystal in such a direction that no Bragg reflection occurs.[1] Other things being equal, the secondary extinction for a powder composed of large crystallites is *less* than that for a powder composed of small crystallites, because primary extinction will have reduced the amount of energy selectively reflected away. Comparative measurements have been made by B. W. Robinson for anthracene single crystals[2] and powders.[3] He measured the linear absorption coefficients using Cu$K\alpha$ monochromatized radiation; for the powders his measurements were made in and at right angles to the direction of compression, and corrected to the single crystal density. His results were:

| | |
|---|---|
| Single crystal ... ... ... ... ... ... | 0·503 per mm. |
| Roughly powdered briquette ... ... ... ... | 0·508 „ |
| Briquette of fine precipitated powder, composed of particles $1–2 \times 10^4$ Å.U. diameter, very uniform ... ... | 0·547–0·558 „ |

Unit area, thickness $t$, of a powder plate, reflects away a proportion of the incident beam equal to $\Sigma\Sigma\frac{1}{2}(Q_0 p \cos\theta).t$, where $Q_0$ is the energy reflected away per unit volume per unit energy of the incident beam, by a very small crystal element; $\rho$ is the number of planes in the form contributing to each reflection, and $\theta$ is the Bragg angle. This will be equivalent to an additional linear absorption $\epsilon$ where $1-\Sigma\Sigma\frac{1}{2}(Q_0 p \cos\theta).t = e^{-\epsilon t}$. $\epsilon$ is therefore of the order of $\Sigma\Sigma\frac{1}{2}(Q_0 p \cos\theta)$. For diamond powdered finely, this would mean an increase of linear absorption coefficient from $13{\cdot}5_0$ to $13{\cdot}8_8$ per cm. for Cu$K\alpha$ and from $1{\cdot}79_3$ to $1{\cdot}93_6$ per cm. for Mo$K\alpha$ radiation.

[1] R. Brill, H. G. Grimm, C. Hermann, and C. Peters, Ann. Physik, 1939, vol. 34, p. 418.
[2] B. W. Robinson, Proc. Roy. Soc. London, Ser. A, 1933, vol. 142, p. 422.
[3] B. W. Robinson, ibid., 1934, vol. 147, p. 467.

This leads to the question as to whether the absorption coefficient values given in such lists as those of the International Tables for Crystal Structure Determination (Berlin, 1935, vol. 2, pp. 575–585) are the correct values to use for single-crystal work. The evidence suggests that, in general, they are not, for practically all the original measurements were made on powdered material, either in the form of briquettes or of metal foil or sheet. As will be shown later, however, the error introduced by using these values is not serious compared with those due to *unsuspected* crystal perfection. The allowance for secondary extinction in the reflecting power of a powdered specimen is made automatically if the coefficient of linear absorption *measured on the specimen itself* enters into the formula for reflection (as it does in the case of reflection from the surface of a powder briquette). Unlike secondary extinction in a mosaic single crystal, secondary extinction in a powdered specimen is independent of the particular reflection considered, because the rays incident on any little block within the specimen will previously have suffered loss of energy by selective reflection in *all* the possible directions. The allowance for secondary extinction must therefore be included in all cases (low or high orders) where absorption is important at all. For instance, the effect of absorption is very marked in the intensity contours of the Debye–Scherrer lines from cylindrical powder specimens and necessitates careful allowance in work where precision measurements of spacing are required, since the apparent maximum of intensity is by no means at the geometrical centre of each line. Here again the effect of secondary extinction should be included by making absorption measurements on the specimen itself, or on a similar powder.

*Study of extinction by use of a divergent X-ray beam.*

The effect of primary and secondary extinction is particularly notable in *transmission* photographs of single crystals, using a widely divergent beam of characteristic X-radiation.[1] On such photographs there is a background of general plus characteristic radiation on which are *white* lines marking those directions in which differential absorption has occurred, on account of radiation having been reflected away (fig. 1). These lines, however, are not always visible; sometimes the background appears to be uninterrupted by any sort of pattern. The lack of a pattern may be due to incorrect exposure or to unsuitable thickness of the crystal specimen. These can be adjusted by trial or by calculation.

[1] K. Lonsdale, Nature, London, 1943, vol. 151, p. 52; 1944, vol. 153, pp. 22, 433; Phil. Trans. Roy. Soc. London (in press).

Even with a correct exposure and suitable crystal dimensions, however, the pattern of absorption lines may be absent either because the crystal is too perfect (primary extinction), or because it is too imperfect (extinction effects smeared out in all directions). It might be imagined that since primary extinction involves a greatly enhanced absorption coefficient, the absorption lines would be particularly noticeable for a perfect crystal. But it must be remembered that although absorption is *complete* in the particular directions for which total Bragg reflection

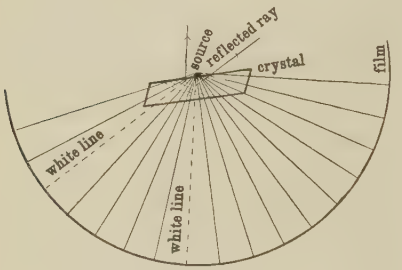


Fig. 1.

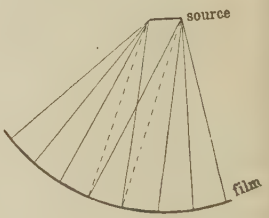


Fig. 2.

Fig. 1. Production of secondary extinction pattern using single crystal and divergent beam.

Fig. 2. Reduction of contrast of sharp absorption in a particular direction, by transmitted rays from another part of extended source.

occurs in an extended perfect crystal, those directions are limited to a few seconds of arc and the proportion of the incident beam absorbed *or* reflected is very small indeed. Also if the source of divergent X-rays is an area instead of an exact point, a sharp absorption in any particular direction will tend to be obscured by transmitted rays of slightly different direction coming from other parts of the source (fig. 2).[1]

In the case of diamond the integrated intensity of reflection $\rho$ from the (111) face of a perfect crystal, using Cu$K\alpha$ radiation, is about $4 \times 10^{-5}$, whereas the corresponding quantity for a mosaic diamond is about $2 \times 10^{-3}$, fifty times as large. The absorption line in the first case (primary extinction) will be much less noticeable than that in the second (secondary extinction). In fact the divergent-beam patterns of white lines are secondary extinction patterns. It is possible to prove this experimentally. If a crystal of an organic compound, such as hexamine or oxalic acid dihydrate, is found to give no divergent-beam pattern,

[1] I am indebted to Dr. W. Ehrenberg of Birkbeck College, London, for this suggestion.

it is possible to make a pattern appear by dipping the crystal into liquid air, a process which would certainly decrease the crystal perfection (R. Brill, *et al.*, 1939, loc. cit.) in an irreversible way. A faint pattern can usually be made more intense by the same procedure. Anthracene is one of the crystals which has been found, by this method, to possess considerable initial perfection in some cases; and this perfection, as has been mentioned before, is not entirely removed by the liquid-air treatment, which does not always have time to break up the crystal on a really small scale before it disintegrates through cracking.

The texture of such crystals as diamond and calcite is not affected by sudden changes of temperature, but it is notable that clear water-white diamonds of obvious perfection do not give a divergent-beam pattern, whereas less perfect specimens (particularly those diamonds known as type II) give good patterns, and the patterns from really distorted diamonds, in which the absorption lines are broad, are usually the most intense of all. The completely mosaic kind of diamond known as *boart* gives no pattern because in this case (as for a powder) all the absorption lines are so broad as to cover the whole film; they are not localized.

Unfortunately, the difficulty of monochromatizing a divergent beam puts *measurement* of secondary extinction by this method out of the question, but the method does give a qualitative idea of the kind and amount of extinction present in any given crystal specimen, and it has shown that both primary and secondary extinction are factors to be reckoned with, even in such relatively soft crystals as those of organic compounds.

*Summary.*—The total absorption and the total scattering from a single crystal or from a crystalline powder are both affected, by primary and secondary extinction, to an extent which varies with crystal texture. The dependence of each on wave-length of X-rays, on perfect crystallite size, and on over-all size of specimen is considered. It is concluded that secondary extinction for a fine powder is greater than that for a coarse powder and that the linear absorption coefficient measured on powdered briquettes or on metal foil is not the correct value to use for single crystal work. Divergent beam transmission photographs give much qualitative information about crystal texture.

# *The cell dimensions and space-group of pinnoite.*

By H. P. Stadler, B.Sc.

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PINNOITE, first described by Staute[1] in 1884, is straw-yellow, granular to faintly fibrous. It occurs in the upper kainite layers at Stassfurt, and is found associated with earthy boracite from which it is freed by washing with water. The analysis corresponds to the formula $MgO.B_2O_3.3H_2O$, and Staute assumes the mineral to be an alteration product of boracite, $6MgO.MgCl_2.8B_2O_3$. Groth classes pinnoite together with $CaO.B_2O_3$ as a hydrated metaborate.[2] This assumption does not seem justified, as will be pointed out later.

Although the mineral appears crystalline, the individual crystals are so firmly intergrown, and the material is so brittle that Staute never succeeded in isolating a crystal with developed faces. This was done later by Luedecke.[3] He ascribes tetragonal symmetry with pyramidal hemihedrism to pinnoite, and from goniometric measurements deduced an axial ratio $c/a = 0{\cdot}7609$. On the specimen available for the X-ray examination discussed in this paper, no crystal with faces could be found. Homogeneous-looking fragments were examined under the microscope. Those that showed no inclusions or wavy extinction were then submitted to X-ray examination by Laue photographs in order to eliminate intergrown crystals. The single-crystal fragments finally selected had to be set entirely by the double oscillation technique. Rotation photographs, using unfiltered Fe or filtered Cu radiation, were obtained about [001], [110], [100], and [201]. A complete set of oscillations (15°) was taken about [110], and absent spectra were specially looked for by long-exposure 5° oscillations about [001], [100], and [201]. The systematic absences so found were $h00$ for $h$ odd, and $00l$ for $l$ odd. The X-ray symmetry $4/m$ is apparent from the oscillation photographs, and was confirmed by a Laue photograph along $c$. This, together with the halving of $00l$, fixes the space-group as $C_4^3 = P4_2$ or $C_{4h}^2 = P4_2/m$. The halving of $h00$ was not required by the space-group, and may be confined to lower orders.

[1] H. Staute, Ber. Deutsch. Chem. Gesell., 1884, vol. 17, part 2, p. 1584.
[2] P. Groth, Chemische Krystallographie. Leipzig, 1908, vol. 2, p. 735.
[3] O. Luedecke, Zeits. Naturwiss. Halle, 1885, vol. 58, p. 646.

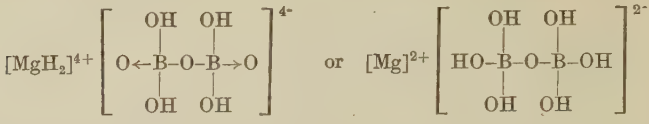
Rough values of the cell dimensions were found from the layer-line distances of the rotation photographs. More accurate values were then obtained by measuring up high-order equatorial reflections with the film in Straumanis position.[1] This eliminates film-shrinkage errors. Absorption of X-rays by this light material is small, and its effect in high orders completely negligible. In this way values $a = 7{\cdot}617 \pm 0{\cdot}002$ Å. and $c = 8{\cdot}190 \pm 0{\cdot}002$ Å. were obtained.[2] They give an axial ratio $c/a = 1{\cdot}075$, which is in good agreement with Luedecke's value, if the different choice of axes is taken into account: thus $c'\sqrt{2} = 1{\cdot}076$. Assuming four molecules per unit cell, the calculated specific gravity is 2·290, in agreement with Larsen's value[3] of 2·29.

The atoms lie in general positions so that all $x$ and $z$ parameters are indeterminate, and a full analysis would be required to find the structure. With no heavy atoms in the molecule this would be an arduous task. The structure of $CaO.B_2O_3$ has, however, been determined by Zachariasen and Ziegler.[4] According to these authors the $B_2O_4$ ion is composed of $BO_3$ triangles. It is thus a chain-ion of the pyroxene type. Since all the atoms of the $BO_3$ triangle lie in one plane, which also contains the chain propagation direction, $CaB_2O_4$ shows a marked birefringence of 0·14, whereas that of pinnoite is only 0·01 ; the length of the repeat unit of the metaborate chain is 4·3 Å., which is far removed from either of the cell dimensions of pinnoite. The double repeat of 8·6 Å. may possibly be fitted into the cell as regards dimensions, but it would have to lie in special positions and symmetry considerations make this impossible.

An alternative to regarding pinnoite as a metaborate would be to write the formula as $Mg(H_2BO_3)_2.H_2O$, i.e. as an acid orthoborate, but there seems to be no positive evidence in support of such a formula. In fact, the behaviour on dehydration opposes both these structures. No water at all is given off below 180° C., suggesting that all the water is present in the form of OH groups. The intermediate products of dehydration showed the same powder pattern as pinnoite on a background of heavy scatter, so that no intermediate crystalline phases appear to be present. This condition of the total absence of water of

[1] M. J. Buerger, X-ray crystallography. New York, 1942, p. 394.
[2] The conversion factor used being 1 kX = 1·00202 Å.
[3] E. S. Larsen and H. Berman, Microscopic determination of nonopaque minerals. Washington, 1934, p. 70.
[4] W. H. Zachariasen and G. E. Ziegler, Zeits. Krist., 1932, vol. 83, p. 354. [M.A. 5–316.]

hydration would be fulfilled by the electronically balanced, but otherwise hypothetical:



As such, it would be the salt of an acid $H_8B_2O_7$, which has neither been described in its free state nor in the form of a salt. In conclusion, therefore, it can only be said that X-ray and chemical evidence make it most unlikely for pinnoite to be a metaborate, but that further work will be required to assign a definite structure to this mineral.

*Acknowledgements.*—The experimental work was carried out at the British Museum of Natural History, with the aid of a research studentship of Birkbeck College. The author wishes to express his thanks to the authorities of the British Museum of Natural History, especially the Keeper of Minerals, Dr. W. Campbell Smith, for granting him facilities to work at the museum, and for providing specimens and materials, and to Mr. F. A. Bannister and Dr. G. F. Claringbull for their constant advice, without which this paper could not have been written.

# *Whitlockite from Sebdou, Oran, Algeria.*

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With a chemical analysis by Miss Hilda Bennett.

[Read June 7, 1945.]

DURING the course of recent work on minyulite ($KAl_2(PO_4)_2(OH,F).4H_2O$) X-ray, optical, and density data were obtained for several hydrous K-Al phosphate minerals.[1] These included one specimen of a soft white compact mineral labelled by P. Pallary as minervite from Sebdou, Oran, Algeria, which was presented in 1940 to the Trustees of the British Museum by Major M. Connolly. Minervite was originally described and analysed in 1895 by A. Carnot from Minerva grotto, Fauzan, dép. Hérault, France.[2] In the same year Carnot also described the same species from Tour-Combes grotto, Misserghin, Oran.[3] Sebdou is some 80 miles SSW. of Oran and geological maps show there a patch of Pliocene on late Jurassic. No doubts were entertained that the specimen under discussion belonged to the same species as minervite from Misserghin, since the geological formations of both localities are closely related. However, no other specimen of minervite could be found in the British Museum collections and Miss Hilda Bennett undertook a chemical analysis of the mineral (table I). This showed at once that it is essentially a phosphate of calcium, and unlike minervite contains no potassium or aluminium. Dr. C. Frondel, on a visit to the Museum, was shown the powder photograph of the analysed mineral and at once recognized that it was identical with that of whitlockite, a new mineral which he described in 1941 from a granite-pegmatite at Palermo quarry, North Groton, New Hampshire.[4]

The specific gravity and optical data are in close agreement with this identification and the powder data are identical with those of Frondel[5]

[1] L. J. Spencer, F. A. Bannister, M. H. Hey, and Miss Hilda Bennett, Min. Mag., 1943, vol. 26, p. 309.
[2] A. Carnot, Ann. des Mines, 1895, ser. 9, vol. 8, p. 319.
[3] A. Carnot, Compt. Rend. Acad. Sci. Paris, 1895, vol. 121, p. 153.
[4] C. Frondel, Amer. Min., 1941, vol. 26, p. 145. [M.A. 8–52, 99.]
[5] C. Frondel, Amer. Min., 1943, vol. 28, p. 215. [M.A. 9–33.]

for whitlockite and of Bredig et alii[1] for artificial $\beta$-$Ca_3(PO_4)_2$. Frondel has also described four other occurrences of whitlockite, including martinite, the carbonate variety from insular phosphate deposits. The mineral is a rare one and this note records an African occurrence for the species.

TABLE I. Chemical analyses of whitlockite.

| | 1. | 2. | 3. |
|---|---|---|---|
| $P_2O_5$ ... ... | 45·87 | 45·68 | 45·78 |
| CaO ... ... | 48·15 | 46·90 | 54·22 |
| MgO ... ... | 3·53 | 2·53 | |
| $SiO_2$ ... ... | 0·04 | — | |
| $Al_2O_3$ ... ... | 0·06 | — | |
| $Fe_2O_3$ ... ... | 0·05 | 1·73 | |
| FeO ... ... | — | 1·91 | |
| MnO ... ... | 0·01 | — | |
| $H_2O+$ ... ... | 1·79 | 0·48 | |
| $H_2O-$ ... ... | 0·21 | | |
| | 99·71 | 99·80 | |
| sp.gr. ... ... | 2·96 | 3·12 | 3·19 (calc.) |
| $\omega$ ... ... | 1·616 | 1·629 | 1·622 (obs.)[2] |
| $\epsilon$ ... ... ... | | 1·626 | 1·620 ,, |

1. Whitlockite, Sebdou, Oran, Algeria, B.M. 1940,98; analysed by Miss Hilda Bennett; Cl trace, $(NH_4)_2O$ trace, $Na_2O$, $K_2O$, BaO, $CO_2$, F not detected.

2. Whitlockite, Palermo quarry, North Groton, New Hampshire, analysed by F. A. Gonyer; also F 0·06, insol. 0·51%.

3. Theoretical figures for $Ca_3(PO_4)_2$.

[1] M. A. Bredig, H. H. Franck, and H. Füldner, Zeits. Electrochem., 1932, vol. 38, p. 158. [M.A. 5–318.]

[2] H. Schneiderhöhn in G. Trömel, Mitt. Kaiser-Wilhelm Inst. Düsseldorf, 1932, vol. 14, p. 35.

# *The identity of minervite and palmerite with taranakite.*

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[Read January 24, 1946.]

THE abundance of the well-known potassium aluminium silicate minerals, orthoclase, microcline, and muscovite, stands in striking contrast with the rarity of the little-known potassium aluminium phosphate minerals. The only one of these which occurs as distinct crystals and which has yielded a satisfactory formula is minyulite, $KAl_2(PO_4)_2(OH,F).4H_2O$. This mineral was first described by E. S. Simpson and LeMesurier[1] from Western Australia in 1933 and an examination of well-crystallized specimens from South Australia by L. J. Spencer et alii[2] was published in 1943. Spencer's paper included X-ray single-crystal and powder data for minyulite. X-ray, optical, and specific gravity data were also determined at that time for a few other hydrous potassium aluminium phosphate minerals from the British Museum collections. These included palmerite from guano deposits in a large cavern, Monte Alburno, near Controne in Salerno, Italy, presented by E. Casoria[3] who described the mineral in 1904, and taranakite from the Sugarloaves, near New Plymouth, Taranaki, New Zealand. A specimen labelled minervite from Oran proved to be whitlockite $\beta$-$Ca_3(PO_4)_2$ and is the subject of the work described in the preceding paper. Only recently did one of the authors (G. E. H.) present a specimen of minervite to the British Museum which is part of a gift he received from Professor P. F. Kerr of Columbia University; this like the original minervite described by A. Carnot[4] is from Minerva grotto, Fauzan,

[1] E. S. Simpson and C. R. LeMesurier, Journ. Roy. Soc. Western Australia, 1933, vol. 19 (for 1932–33), pp. 13–16. [M.A. 5–293.]

[2] L. J. Spencer, F. A. Bannister, M. H. Hey, and Miss H. Bennett, Min. Mag., 1943, vol. 26, pp. 309–314.

[3] E. Casoria, Atti R. Accad. Georgofili, Firenze, 1904, ser. 5, vol. 1, p. 293; Ann. R. Scoula Sup. Agric. Portici, 1904, vol. 6.

[4] A. Carnot, Ann. des Mines, 1895, ser. 9, vol. 8, p. 319.

dép. Hérault, France. These specimens are the principal ones which we have studied and upon which we base our identification.

Despite the differences in the published chemical analyses of these minerals, all three yield the same X-ray powder photographs and have almost identical refractive indices and specific gravities. Taranakite is a pale-cream compact mineral occurring as thin seams in the trachytic rocks of the Sugarloaves. Prior to chemical analysis it was thought to be wavellite, but it is softer and more readily fusible.[1] Hector and Skey observed a few thin seams of a dark yellowish-brown coloured substance traversing the taranakite in various directions. They reported these seams to be wavellite and said they avoided them in selecting a sample of taranakite for chemical analysis. We have detected the same inclusions and have shown by X-ray powder photographs that they are identical with vashegyite, not wavellite.

Both palmerite and minervite are soft, powdery minerals like kaolin in appearance and to the touch. Like taranakite they are very fine-grained, but when immersed in a liquid and viewed with an inch objective they reveal minute birefringent laths. Their refractive indices obtained by the Becke line method are given in table I. Molecular proportions calculated from published chemical analyses are also listed

Table I. Chemical analyses and molecular ratios.

| | I. | II. | III. | | I. | II. | III. |
|---|---|---|---|---|---|---|---|
| $P_2O_5$ ... ... | 35·05 | 37·28 | 37·10 | ... | 3·0 | 3·0 | 3·0 |
| $Al_2O_3$ ... ... | 21·43 | 18·59 | 22·89 | ... | 2·89 | 2·14 | 2·79 |
| $Fe_2O_3$ ... ... | 4·45 | 0·83 | 1·17 | | | | |
| CaO ... ... | 0·55 | 1·40 | trace | | | | |
| $K_2O$ ... ... | 4·20 | 8·28 | 8·04 | ... | 0·54 | 1·00 | 0·98 |
| $(NH_4)_2O$ ... ... | — | 0·52 | 0·90 | | | | |
| $H_2O$ ... ... | 33·06 | 28·20 | 29·16 | ... | 22·29 | 17·88 | 18·59 |
| Insol. ... ... | 0·80 | 4·35 | 0·36 | | | | |
| | 100·00 | 99·78 | 99·64 | | | | |
| Sp.gr. ... ... | 2·15 | — | 2·15 | (F.A.B.) | | | |
| $n$ ... ... | 1·502 | 1·50 | 1·507 | | | | |

I. Taranakite, Sugarloaves, Taranaki, New Zealand. Also $Na_2O$ trace, Cl 0·46, $SO_3$ trace, iron as FeO. (Hector and Skey, 1865.) Specific gravity and optical data on B.M. 1936,51.

II. Minervite, Minerva grotto, France. Also MgO 0·33. F, Cl, $SO_3$ traces. (A. Carnot, 1895.) Optical data on B.M. 1947,1.

III. Palmerite, Monte Alburno, Italy. Also $Na_2O$ 0·02, MgO trace. (E. Casoria, 1904.) Specific gravity and optical data on B.M. 1909,370.

[1] J. Hector and W. Skey, Reports of the Jurors, New Zealand Exhibition, 1865, Dunedin, 1866, p. 423. S. H. Cox, Trans. New Zealand Inst., 1882, vol. 15, p. 385.

in the same table. Palmerite and minervite have yielded analyses not incompatible with their identity if one admits the possibility of admixture of small quantities of other undetected minerals. Taranakite, however, apparently possesses only half the potash content of the other two and, if we attribute this to admixture with vashegyite, then we must conclude that despite their care in selecting material for analysis Hector and Skey actually analysed a mixture of taranakite and vashegyite in about equal proportions. There is, however, too little vashegyite present in the specimen of taranakite that we have examined to support this assumption. It would be more reasonable to assume that their figure for potash is low owing to their failure to separate all the enclosed vashegyite, and that the differences in composition between taranakite, minervite, and palmerite, particularly their variation in content of potash, remain for the present unexplained. The X-ray powder data (table II) and optical data do, however, show that the

TABLE II. Spacings in kX units and estimated intensities of the lines observed on X-ray powder photographs of taranakite, B.M. 1936,51, taken with filtered copper radiation, 1·539 kX, in a cylindrical camera, 5·98 cm. diameter.

| | | | | | |
|---|---|---|---|---|---|
| 15·5 vs | 3·34 mw | 2·19 w | 1·68 vw | 1·396*vw | 1·209 w |
| 7·6 s | 3·15 s | 2·07 ms | 1·65 vw | 1·354 vw | 1·172 w |
| 5·8 m | 2·84 s | 1·97 mw | 1·61 mw | 1·338 vw | 1·146 vw |
| 5·1 vw | 2·73 vw | 1·91 w | 1·569 vw | 1·316 vw | 1·133 vw |
| 4·39 m | 2·63 ms | 1·88 vw | 1·542 vw | 1·281 w | 1·115 vw |
| 3·82 s | 2·40 m | 1·84 ⎫ mw | 1·502 mw | 1·262 vw | 1·097*vw |
| 3·58 m | 2·26 w | 1·77 ⎭ mw | 1·466 vw | 1·246 w | 1·073 vw |
| | | 1·73 mw | 1·427 mw | 1·237 vw | 1·056 vw |

Bracketed lines are unresolved bands consisting of several lines, and the diameters and intensities of the limits are given.

* Doublets.

main component of the three specimens we have examined is the same, and on grounds of priority we consider that all three should be named taranakite. Only an approximate formula can be given, and this we base on Casoria's analysis of palmerite rather than on the much earlier analysis of taranakite itself. Casoria's analysis yields approximately $3P_2O_5.3(Al,Fe)_2O_3.K_2O.18H_2O$. Our choice is arbitrary and assumes a comparatively simple formula and a constant composition.

THE GEOCHEMISTRY OF TARANAKITE (G. E. Hutchinson).

A qualitative spectrographic examination of the specimen of minervite showed strong lines of K, Al, and Fe, as would be expected from the published analyses; Na, a small amount of Ca, and a trace of Mg were

also present. Rb is definitely present in more than minute traces, the concentration being possibly of the order of 1% of the K-content; this may be of some interest as suggesting that the potassium as well as the aluminium of the mineral came from the rock undergoing alteration rather than from the guano solution. Li, Sr, Ba, Mn, and Zn appear to be absent, though the conditions for recognizing the last element were poor. Pb is definitely present, but in view of the fact that the powdery mineral had been lying for many years in a drawer in New York City, the lead may be a contaminant. The material appears to contain no exchangeable hydrogen or exchangeable bases.

The name minervite has been given to material from various localities similar to that from Minerva grotto, Fauzan, France. Published analyses suggest that many of these are also identical with taranakite and the known and probable occurrences of the mineral may be grouped as those of:

(1) Caves, probably due to phosphatizing solutions from bat guano, which, however, may have disappeared.—Grotte de Minerve, France (minervite, A. Carnot, 1895); Monte Alburno, Italy (palmerite, E. Casoria, 1904); Misserghin, Algeria ('minervite', A. Carnot, 1895);[1] Jenolan, New South Wales ('minervite', J. C. H. Mingaye, 1898);[2] Réunion, Indian Ocean ('minervite', A. Lacroix, 1910).[3]

(2) Coastal localities, probably due to phosphatizing solutions from bird guano.—Sugarloaves, Taranaki, New Zealand (taranakite, Hector and Skey, 1866); Islas Leones, Patagonia (L. R. Catalano).[4]

It will be observed that both the coastal localities are in relatively high latitudes. In tropical latitudes in which the phosphatization of the igneous rocks of bird-islands has occurred, the resulting minerals appear to be variscite and metavariscite ($AlPO_4.2H_2O$), barrandite ($(Al,Fe)PO_4.2H_2O$), strengite and phosphosiderite ($FePO_4.2H_2O$). Such occurrences have been described by Lacroix[5] and by McConnell[6] and less critically by many other authors. A full discussion of all localities will appear in a later publication on the biogeochemistry of guano deposits (Hutchinson, forthcoming). Meanwhile it is desirable to point out that the known

[1] A. Carnot, Compt. Rend. Acad. Sci. Paris, 1895, vol. 121, p. 153.

[2] J. C. H. Mingaye, Rep. Australasian Assoc. Adv. Sci., 1898, vol. 7, p. 327; Rec. Geol. Surv. New South Wales, 1899, vol. 6, p. 113.

[3] A Lacroix, Bull. Soc. Franç. Min., 1910, vol. 33, p. 34; 1912, vol. 35, p. 114.

[4] L. R. Catalano, Argentina Direc. Minas y Geol. Pub., 1933, no. 100, p. 1. Analysis of nodular phosphate from Islas Leones yielded a formula near to that of palmerite.

[5] A. Lacroix, Compt. Rend. Acad. Sci. Paris, 1906, vol. 143, p. 661.

[6] D. McConnell, Rev. Colegio Ing. Venezuela, 1941, vol. 19 (no. 140), p. 115; Bull. Geol. Soc. Amer., 1943, vol. 54, p. 707. [M.A. 9–182.]

distribution of the $(Al,Fe)PO_4.2H_2O$ minerals confirms the suggestion of Lacroix that they occur in regions of markedly seasonal rainfall. Such regions are characterized on land by 'la latérisation, cette autre maladie tropicale des roches silicatées' (Lacroix, 1906, loc. cit.). In contrast to this it is reasonable to suppose that the two exposed and all the hypogean sites of formation of taranakite are perennially damp. The Sugarloaves, as illustrated in the New Zealand Pilot (U.S. Hydrogr. Office no. 171, 1929, view 20), appear to be ideal sites for bird colonies. Though it seems improbable that the islands are at present occupied by large numbers of birds, Morgan[1] indicates that the phosphorus of the taranakite and the wavellite found on these islands is undoubtedly of avian origin. The Islas Leones material which is chemically similar, but otherwise little known, is associated with a penguin colony. In view of the considerable climatic differences between the west coast of New Zealand, off which the Sugarloaves lie, and the drier east coast, a critical examination of the so-called Redonda phosphate of Green Island and White Island, Otago, would be interesting. The supposed titanium phosphate (Morgan),[1] apparently found as the result of phosphatization by guano solutions at Antipodes Island, also requires investigation.

Finally, it may be pointed out that if one is justified in supposing that taranakite is the typical product of phosphatic alteration in perenially damp conditions, small amounts may well be present dispersed in wet soils, and that the possible formation of such a mineral should be considered by investigators interested in the fate of soluble phosphates added to soils.

[1] P. G. Morgan, Réserves mondiales en Phosphates. Congrès Géol. Internat. 1926, Madrid, 1928, vol. 2, p. 823.

# *The nomenclature of the halloysite minerals.*

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[Read June 6, 1946.]

THE name 'halloysite', first used in 1826 by Berthier (1), is derived from that of Omalius d'Halloy, who found the mineral in Angleur, Liége, Belgium. In 1935, Mehmel (2) discovered that there were two distinct substances included under the name halloysite, one of which contains loosely bound water and shows a 10 Å. basal reflection on an X-ray diagram, the other none and shows a reflection at about 7 Å. Mehmel preserved the name halloysite for the hydrous mineral, and for the product of its dehydration he proposed the name 'metahalloysite'. Both substances may occur naturally (though this may not have been known to Mehmel at the time). Previous to this work it had been suggested by Hofmann, Endell, and Wilm (3) that the 10 Å. material on dehydration at a low temperature gave kaolinite. Mehmel showed that this was wrong; and that the error was due to the similarity of the X-ray diagrams of kaolinite and metahalloysite. Hofmann and co-workers, and Mehmel, all tacitly assumed that the name halloysite was correctly applied to the 10 Å. material rather than the 7 Å. material.

In the United States, the practice introduced by Hendricks (4) of using 'halloysite' for the *non*-hydrated material and 'hydrated halloysite' for the hydrated material has usually been followed in recent years. This practice never became universal; and in fact all three terms continued in use, with 'halloysite' used in both senses. Recently in America yet another revision of the nomenclature has been proposed, in an attempt to clear up the confusion. This consists in the introduction of a new name 'endellite' (5) for the hydrated mineral, the name 'halloysite' being retained for the dehydrated mineral. This nomenclature has been adopted in another recent American paper (6). In the present note I wish to point out that this suggestion has found little favour among workers on clay minerals in this country; to present the arguments against it; and to suggest a convenient nomenclature which takes account of recently discovered properties of the halloysite minerals.

The introduction of the name 'endellite' would mean adding to the already overloaded mineralogical terminology. The name has no obvious connexion with halloysite, so that, in effect, if it were adopted, three separate acts of memory would be required of students (i.e. the two names for the hydrated and non-hydrated forms, and the fact of their—undoubted—close connexion in nature) instead of one (or one and a fraction). The new name might be justified if it stood for a completely distinct substance. But does it? I wish to suggest that recent research has shown that halloysite and metahalloysite (hydrated halloysite and halloysite: or endellite and halloysite) are so closely connected that they are more conveniently regarded as two aspects of a single substance than as entirely separate substances.

The picture of the halloysite structure which emerges from recent work is this (5–8). The hydrated form of the mineral consists of kaolinite sheets interspersed with monomolecular sheets of water molecules. There is no regularity detectable by X-rays in the packing of the sheets, apart from the constant distance between them, measured in a perpendicular direction. In conformity with this idea of a structure of very high energy, the structure is a very labile one, and the water layer may readily be replaced by a layer of other polar molecules, e.g. ethylene glycol, glycerol, methanol, &c. On dehydrating halloysite at low temperatures, the water sheets are lost, but the kaolinite sheets remain intact, and come into contact with each other, becoming linked by O-H–O bonds. The energy of this inter-sheet linkage depends on the exact treatment of the specimen, and though some specimens of metahalloysite will give the glycol compound on treatment with glycol, others will not. Thus the following points are clear:

(*a*) The hydrated form of halloysite ('endellite') is only one of a number of possible complexes in which the large kaolinite sheets are interspersed with monomolecular layers of polar molecules.

(*b*) Metahalloysite is a substance of doubtful uniformity and may show various degrees of energy of binding of the structural sheets.

In addition, it may be mentioned that:

(*c*) Naturally occurring halloysite minerals may be intermediate between the hydrated halloysite ('endellite') and the non-hydrated halloysite ('metahalloysite') (this fact is supported by published analyses, mentioned below, and also by X-ray diagrams which I have made of natural halloysites).

These facts make it clear that the two halloysite minerals are only two members of a series of substances which includes various intermediate

forms, as well as forms in which water of hydration is replaced by other molecules. The situation is very similar to that arising in connexion with the mineral montmorillonite. Like halloysite, this has a highly irregular structure, with mobile inter-sheet molecules. The hydrated forms of montmorillonite may be irreversibly dehydrated by heating (to 200° as against 50° for halloysite), though according to Bradley (9) it may then still be rehydrated via the glycol compound (cf. similar behaviour of halloysite (7)).

In describing this mineral the usual practice (seldom explicitly stated) has been to use one name 'montmorillonite' to cover all its possible forms, with various quantities of water or other molecules. The name 'montmorillonite' is thus regarded as a general name covering various particular forms; these have been more precisely designated as hydrated montmorillonite, glycerol-montmorillonite, &c. This seems the only reasonable procedure with such a reactive substance.

My suggestion is that the same procedure be adopted in the case of halloysite. Thus the name 'halloysite' would be taken to cover all the naturally occurring halloysite minerals (hydrated, non-hydrated, and intermediate) as well as artificially produced complexes; and for particular forms the precise terms 'hydrated halloysite', 'glycerol-halloysite', &c. would be used (whether these were obtained starting from the hydrated or the non-hydrated form). The convenient term 'metahalloysite' would be retained for the non-hydrated form (with the understanding that it is only an approximative term, and that the material thus described may not be uniform). It is contended that this suggestion provides a logical, coherent nomenclature for all the manifestations of the halloysite minerals, particularly for the organic complexes. The 'endellite-halloysite' system of nomenclature breaks down rather badly when dealing with these. The glycerol complex, for instance, is generally obtained starting with 'endellite'. Is it therefore to be called 'glycerol-endellite'? This seems wrong because the term endellite suggests the presence of water molecules, which do not occur in the glycerol complex. If the term 'glycerol-halloysite' is to be used, then the case for 'hydrated halloysite', and thus for the whole system of nomenclature proposed here, seems to be admitted ('hydrated halloysite' is misleading if 'halloysite' is taken to mean metahalloysite, for metahalloysite cannot generally be hydrated (10); but correct if halloysite is understood as a general term).

It is perhaps desirable to discuss briefly here how the usage suggested above fits in with the historical use of the name 'halloysite', since there

seems to have been as much confusion over this as over the other aspects of the nomenclature. When Hendricks proposed his first system of nomenclature (4) (i.e. 'halloysite' in the sense of metahalloysite, and 'hydrated halloysite') he stated that 'as a rule, Mehmel's metahalloysite is the usual halloysite of others'. No references were cited to support this statement. In a later summarizing paper on the clay minerals, Grim (11) went still farther, and stated that 'Hendricks has suggested the names "hydrated halloysite" and "halloysite", respectively, for these minerals [i.e. hydrated and metahalloysites], thus retaining the name "halloysite" for material of the composition to which it was first applied'. Alexander and others, in the introduction of their paper (5), implicitly support the idea that the original usage of the term 'halloysite' was identical with that of Hendricks's.

I believe that, in fact, Hendricks's original statement is very doubtful, and Grim's definitely incorrect. The accompanying table gives a list of analysed samples of halloysite, derived from papers published before 1934 (the date of the Ross and Kerr paper mentioned below), together with the total number of molecules of water in the formula for the air-dry or lightly dried material, as quoted by the authors or deduced from their data (based on one $Al_2O_3$ group per formula: but analyses were rejected for which the $SiO_2 : Al_2O_3$ ratio differed markedly from 2). This number should be 2 for meta-, and 4 for hydrated halloysite: a glance at the table shows that in most cases it is nearer to the latter than the former, though practically the whole intermediate range is covered. Le Chatelier (19) in particular analysed a large number of halloysite specimens, and distinguished between water lost above and below 250° C. His results correspond to formulae varying from $Al_2O_3.2SiO_2.2H_2O + \frac{1}{2}H_2O$ to $Al_2O_3.2SiO_2.2H_2O + 2\frac{1}{2}H_2O$, the second group of water molecules representing the more loosely bound water. It was perhaps this paper, with its emphasis on the method of differential thermal analysis, introduced by Le Chatelier, which resulted in a widening of the connotation of the term 'halloysite' to include various minerals which gave essentially the same type of differential thermal diagram. In the earlier literature, there were a number of different names for material which was probably essentially halloysite, and a few of these are given in the table. It shows incidentally that the name 'lenzinite' really has priority, for it was used by J. F. John (12, 13) in 1816 to describe a material essentially the same in composition as the hydrated variety of halloysite. However, the name 'lenzinite' got applied to a number of ill-defined materials of widely varying composition, so its demise is understandable.

*Table of water-content data from halloysite analyses.*

This table lists halloysite analyses made before 1934; although not claimed to be exhaustive, it probably gives a fair sample, and should include all the important ones. The total number of molecules of water in the air-dry or lightly dried material is given in each case, together with the locality of origin, the analyst (not necessarily the same as the author of the paper), and the name under which the mineral was described if different from 'halloysite'.

| | Mols. $H_2O$. |
|---|---|
| 'Lenzinite argileuse' (John, 1816) (12) | 4·0 |
| 'Lenzinite', Eifel, Germany (John, 1816) (13) | 3·8 |
| Angleur, Belgium (Berthier, 1826) (1) | 4·4 |
| Lavoulte, France (Dufrénoy, 1833) (14) | 4·2 |
| Thiviers, France „ „ „ | 3·9 |
| Miechowitz, Silesia (Oswald, 1837) (15) | 3·9 |
| 'Glossecollite', Dade Co., Georgia (Pisani, 1861) (16) | 3·2 |
| 'Indianaite', Indiana (Pemberton, 1878) (17) | 3·7 |
| Drenkova, Banat (Helmhacker, 1880) (18) | 3·5 |
| „ „ „ „ „ | 4·5 |
| Brandberg, Germany „ „ „ | 4·5 |
| Eifel, Germany (Le Chatelier, 1887) (19) | 2·4 |
| Laumède, France „ „ „ | 2·6 |
| Huelgoat, France „ „ „ | 2·6 |
| Miglos, France „ „ „ | 3·1 |
| Russia „ „ „ | 3·2 |
| Angleur, Belgium „ „ „ | 3·6 |
| Breteuil, France „ „ „ | 4·2 |
| 'Indianaite', Indiana (Noyes, 1904) (20) (cf. Pemberton's analysis, above) | 2·2 |
| Kolyvansky mine, Altai (Pilipenko, 1915) (21) | 2·5 |
| Wagon Wheel Gap, Colorado (Larsen and Wherry, 1917) (22) | 3·8 |
| Radzionkow, Silesia (Šplíchal, 1919) (23) | 2·7 |
| Angleur, Belgium „ „ | 3·7 |
| Worm's Heath, Surrey (Edge, 1919) (24) | 3·4 |
| Djebel Debar, Algeria (Granger and Brémont, 1922) (25) | 4·0 |
| Kedabek, Elizavetpol (Chirvinsky, 1929) (26) | 4·1 |
| Elbingerode (Erdmannsdörffer, 1930) (27) | 4·9 |

Statements abound in the earlier literature to show that the analysts were well aware of the existence of additional loosely bound water in the samples they examined. As an example, Helmhacker's important paper (18) may be cited. He points out that at 100° C. the formula of halloysite approaches that of kaolinite, but shows considerably more water at lower temperatures. The formula given by Rammelsberg in his 'Mineralchemie' (28) shows four molecules of water, though he wrongly suggests that three of these are more loosely combined than the other one. Larsen and Wherry in their paper (22) put forward the formula $Al_2O_3.2SiO_2.2H_2O+2aq$. It is true that in the more recent series of analyses of halloysites mostly of American origin, quoted by

Ross and Kerr (29), the amount of water found in excess of the theoretical value for metahalloysite is always small, and it may be on the authority of this important paper that the American practice of using 'halloysite' for metahalloysite has arisen. Ross and Kerr, however, were not aware of the nature of the hydrated form of halloysite, and cannot therefore have known of the importance of guarding against the loss of the inter-sheet water. The pre-treatment used on their samples was not specified, but may have resulted in this water being driven off. In this connexion, Hendricks's statement (4) is interesting, that this water was lost (as shown by X-ray photographs) on exposure to the laboratory air for one week. This is not true of the perhaps relatively under-heated laboratories in this country according to my experience (confirmed by others).

In the original paper of Berthier (1), the 'analysis of halloysite' which he quotes would lead to the formula $Al_2O_3.2SiO_2.4{\cdot}4H_2O$. There can be no doubt therefore that the type material was hydrated halloysite. Šplíchal's (23) and Le Chatelier's (19) analyses of material from the same locality also correspond to hydrated halloysite (3·7 and 3·6 $H_2O$ respectively). The adoption of the 'endellite' nomenclature would thus mean giving a new name to material identical with Berthier's original 'halloysite'. It is true that Berthier states that the 'true composition' of halloysite is probably '$2AlS^2 + AlAq^2$'; or, in modern symbols, $Al_2O_3.2SiO_2.2H_2O$. This formula, however, is based on the supposition that the water lost below 100° C. is not to be regarded as part of the structure. Berthier makes it clear that this supposition is only tentative, by referring specifically to the difficulty of deciding what part of the water is to be regarded as definitely bound. In choosing a 'theoretical' formula he may also have been influenced by a now-defunct theory of 'chemical types'; the analyses furnish no justification for splitting the alumina into two parts. The difficulty of classifying the low-temperature water is one which has persisted until to-day, for it occupies a peculiar intermediate position between 'adsorbed' and 'combined' water. As regards energy and type of binding it resembles the former; but the series of adsorption complexes, of which hydrated halloysite is one, have a more clearly defined individuality than most. The proposed nomenclature takes account of this fact by giving them separate, but not unconnected, names.

Hofmann and co-workers, and Mehmel, were historically correct in assuming that the hydrated halloysite was the true halloysite, so that Mehmel's nomenclature is better justified than Hendricks's, or the 'endellite' nomenclature. I believe, however, that the system I have

suggested is really the best historically as well as from the point of view of modern knowledge. Its adoption would mean that everything which has been called 'halloysite' in the earlier literature (obvious errors excepted) could still be called halloysite; the qualifying prefixes 'hydrated', 'partly hydrated', or 'meta' being added only if required. In soil work the proposed nomenclature will be valuable, for it will enable a measure of vagueness to be introduced into descriptions where it is unavoidable, and precision, devoid of cumbrous terminology, where it is justified. Ideally, of course, soil-clay mineralogists should be able to say of any sample whether it is hydrated halloysite ('endellite'), metahalloysite, or something intermediate. In practice, however, there may often be doubt whether the pre-treatments used on the clay may not have resulted in hydrated halloysite being altered to metahalloysite. The term 'halloysite', covering both minerals, may then be used; as has in fact often been done in the past, though not always explicitly stated. Dr. L. J. Spencer (Min. Mag., vol. 26, p. 336) agrees with my criticisms of Hendricks's nomenclature, and the 'endellite' nomenclature, but would prefer the term 'halloysite' to be confined to the fully hydrated variety. As a soil-clay worker, I think that such a specific use of 'halloysite' would be difficult to observe consistently in practice.

The possibility must be considered that there exist minerals which are intermediate between (meta) halloysite and kaolinite, i.e. less regular than kaolinite, but not so irregular as halloysite (30). Such minerals, in their relation to halloysite, might be similar to certain hydrous micas (6) in relation to montmorillonite. The nomenclature proposed here does not take account of them; obviously more data on their nature and variation must be accumulated before a satisfactory nomenclature is arrived at. The material from Saglik for which Belyankin and Ivanova have used the name 'hydrokaolin' (31) may be of this type; it contains rather more water than normal kaolinite and is birefringent.

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## *Excursion to Durham and the northern Pennines.*

Report by K. C. Dunham, D.Sc., S.D., M.I.M.M.

Geological Survey of Great Britain.

THE decision of the Council to organize an excursion, the first since the Jubilee of the Society in 1926, arose from an invitation presented by Dr. A. E. J. Vickers, on behalf of Imperial Chemical Industries Ltd., to visit the anhydrite mine at Billingham. During the excursion the opportunity was also taken of visiting mineral localities in the northern Pennines (west Durham and Cumberland) under the leadership of Professor Wager and the writer. Accommodation was arranged in Durham at University College (by kind permission of the Master), and here, housed in the ancient castle, members enjoyed a comfortable stay. Transport each day was by private coach. The excursion was organized by Dr. G. F. Claringbull; the thanks of members are also due to Mr. E. Myers, secretary of the north-east section of the Society of Chemical Industry for his help in making local arrangements.

The following attended: The President, Dr. W. Campbell Smith (London), W. Anderson (Newcastle), P. D. Blake (Manchester), G. F. Claringbull (London), K. C. Dunham (London), J. Drugman (Liége), T. J. Duffy (Dublin), R. C. Evans (Cambridge), G. S. Gowing (Billingham), Mrs. K. Lonsdale (London), D. M. C. MacEwan (Harpenden), G. H. Osborn (Aylesbury), J. V. Ramsden (Honiton), J. E. Richey (Edinburgh), L. J. Spencer (London), R. C. Spiller (Oxford), F. H. Stewart (Durham), J. H. Taylor (London), S. I. Tomkeieff (Newcastle), A. E. J. Vickers (Billingham), L. R. Wager (Durham), R. C. Walsh (Blackpool), D. G. A. Whitten (Billingham), Miss D. E. Wisden (Newcastle), J. D. H. Wiseman (London).

The party assembled in Durham on the evening of 1st July.

*Tuesday, 2nd July.*—The main objective on the first day was the Rotherhope Fell lead mine, near Alston, Cumberland. The route followed took the party across the western part of the Durham coalfield to Tow Law, formerly the site of an important iron industry smelting ores from the Pennine metalliferous veins, but now derelict. Thence the 'Millstone Grit' was crossed and between Wolsingham and the head of Weardale rocks of the Upper and Middle Limestone groups of the Carboniferous Limestone Series could be seen making terrace-like features

on the hillsides. The Cumberland border was crossed at the pass of Killhope (2056 feet), where the Wear River rises, and passing through Nenthead and Alston, Rotherhope Fell mine, situated on the Black Burn, a tributary of the South Tyne, was reached.

At the mine, which is owned by the Vieille Montagne Zinc Co. Ltd. (Manager, Mr. Amos Treloar, J.P., M.I.M.M.), the party was conducted

Fig. 1. Rotherhope Fell lead mine.
(Photo. by Dr. G. F. Claringbull.)

round the workings by Mr. G. Robinson. The deposits consist of metasomatic flats replacing the Tynebottom Limestone (Middle Limestone Group: 22 feet thick), on both sides of the ENE. Rotherhope Vein. The quartz-dolerite Whin Sill, here 180 feet thick, directly underlies the limestone, and vein-oreshoots were formerly worked in the sill at this mine. The minerals in the flats include chalcedony, opal, quartz, fluorite, galena, blende, marcasite, chalybite, ankerite, and calcite. The flats occur beneath a flat-topped anticline which follows the vein, and are clearly related to minor fissures which diverge from it.

We rode (fig. 1) into the mine by way of the Blackburn Level, engineered by Smeaton in 1837. The level runs southward as a crosscut through a shallow syncline in the 'Alternating Beds' (above the Tyne-

bottom Limestone); we noted a minor waterfall where Victoria Vein was cut by the level. On reaching Rotherhope Vein, the level runs WSW. From this the north side flats were reached by way of an incline, and pillars typical of the deposit were examined. In one of them Mr. Walsh pointed out a pink incrustation of erythrite which he had discovered on a previous visit. From these pillars we proceeded along the north side of the vein to the south-west end of the workings, where crystals of calcite, fluorite, and marcasite were obtained. The incline was then followed down to the south-side flats which lie approximately 35 feet below those on the north side owing to the throw of the vein. Here specimens of 'White Whin', a calcitized, sericitized, and silicified modification of the quartz-dolerite resulting from the action of the mineralizing fluids, were collected.

Lunch was eaten in the sunshine outside the mine, and after a brief visit to the gravity mill where the lead ore is dressed, the journey was resumed. Near Alston a stop was made at the old Blagill mine, the well-known locality for barytocalcite, good examples of which were collected from the dumps. Tea, probably the most memorable meal of the excursion, was taken at the Nenthead Hotel. Nearby is the flotation plant which was erected during the war to recover zinc from the 600,000 tons of dumps at Nenthead; this operation has now been completed.

A final stop was made at the outcrop of Old Moss Vein, in Killhope Burn, which is exposed in the Great Limestone. A channel-sample across this outcrop, taken in 1940, assayed as follows: $SiO_2$ 14·6, total Fe 29·3, Mn 2·3, MgO 1·5, CaO 10·6, $CO_2$ 15·7, Zn 3·2, Pb 1·2, S 1·4, F 3·3 (Geological Survey Lab., No. 1170).

*Wednesday, 3rd July.*—A short journey from Durham brought the party to New Brancepeth colliery, where, by courtesy of the New Brancepeth Coal Co. Ltd. (Manager, Mr. G. S. Watson), we visited the workings on one of the baryte oreshoots associated with the Deerness fault. Before arriving Dr. Spencer[1] recalled the circumstances of his discovery of ullmannite and alstonite at this mine in 1910.

Under the leadership of Mr. A. Harrison and six of his staff, the deposit was reached by way of the colliery shaft, and a somewhat arduous walk along a drift in the Harvey Seam, the highest seam worked at this colliery. It lies in a fault striking ENE. and downthrowing 120 feet N.,

[1] L. J. Spencer, On the occurrence of alstonite and ullmannite in a barytes-witherite vein at New Brancepeth Colliery, near Durham. Min. Mag., 1910, vol. 15, pp. 302–311.

considered to be the continuation of the Coldberry–Sharnberry vein-system of the northern Pennines.[1] The ore-shoot varies up to about 25 feet wide, the filling being baryte, with a little witherite in places, particularly near the walls; an average analysis of monthly shipments during the year ending March 1945 gave $BaSO_4$ 90·28, $BaCO_3$ 2·36, $SiO_2$ 3·64, $Fe_2O_3 + Al_2O_3$ 1·50, $Mn_3O_4$ 0·18, $CaSO_4$ 0·20, Cu 0·013, ZnS 0·31, PbS 0·71, ignition loss 0·86 (from analyses by Athole G. Allen (Stockton) Ltd.). It is worked by a series of levels reached from an underground shaft and winzes below the Harvey coal, and the visit involved climbing numerous ladders. Crystals of baryte and witherite were obtained, and an efflorescence containing nickel-bearing goslarite, first analysed by Dr. J. A. Smythe,[2] was collected; a new examination of one of the samples obtained, made by Mr. G. H. Osborn, showed the presence of 1·9 % $NiSO_4.7H_2O$. Another sample taken by Mr. G. S. Gowing was analysed by Mr. H. N. Redman of Imperial Chemical Industries and showed: $ZnSO_4.7H_2O$ 88·5, $MnSO_4.7H_2O$ 2·6, $FeSO_4.7H_2O$ 4·6, $MgSO_4.7H_2O$ 4·3. Nickel was not present in this sample.

Lunch was taken at the colliery canteen, through the kind permission of the miners' committee, and afterwards the party proceeded by bus to Annfield Plain, where the witherite dressing plant and barium chloride plant of the Holmside and South Moor Colliery Co. were examined. Here our guide was Mr. E. W. Muddiman, B.Sc., F.R.I.C., who has published a description of the mining and treatment of witherite.[3] The ore is mined from a fault in the Middle and Lower Coal Measures; it consists largely of witherite with minor amounts of baryte, pyrite, and calcite. A visit was also paid to Mr. Muddiman's laboratory, where systematic assays of vein- and product-samples are made.

After dinner at the Castle, Professor L. R. Wager took the party round the Geology Department of the Durham Division of the University; a feature of special interest was his material from Greenland. The evening ended with an entertainment at Professor Wager's house.

*Thursday, 4th July.*—Weardale was again visited, the objective being the Stanhopeburn fluorspar mine, north of Stanhope, belonging to Fluorspar Ltd. Here, under the guidance of Mr. W. Herdman, the manager, we were conveyed underground in mine cars, along Shield

[1] K. C. Dunham and H. G. Dines, Barium minerals in England and Wales, Geological Survey Wartime Pamphlet, 1945, no. 46, pp. 64–66.

[2] J. A. Smythe, Nickel-bearing goslarite, epsomite and melanterite from County Durham. Vasculum, 1933, vol. 19, pp. 12–17. [M.A. 5–283.]

[3] E. W. Muddiman, Witherite. Journ. Oil and Colour Chemists' Assoc., 1942, vol. 25, pp. 127–142. [M.A. 8–336.]

Hurst Level. The deposit is a complex of ore shoots on the ramifying branches of the Red Vein, one of the most persistent WNW. veins of the Pennines. Widths of fluorite of about 20 feet occur here, where the veins cut the Great Limestone and the thick underlying sandstone. Minerals present other than fluorite include subordinate amounts of quartz, galena, calcite, ankerite, and marcasite. From Shield Hurst

Fig. 2. At the Castle, Durham.

Drugman, Stewart, Duffy, Blake, Tomkeieff, Osborn, Evans, Dunham, Wager, Taylor, Richey, Wiseman, Walsh, MacEwan, Spiller, Anderson, Ramsden, Campbell Smith, Miss Wisden, Spencer. (Photo. by Dr. G. F. Claringbull.)

level, we descended the Beaumont underground shaft and proceeded through a series of impressive shrinkage stopes, returning to the shaft by way of the 17-fathoms level.

From Stanhope we continued up the valley to St. John's Chapel, then crossed the Harthope pass to Teesdale. Here Mr. Anderson pointed out ganister workings on a siliceous sandstone near the horizon of the Fell Top Limestone. Professor Wager now took over the party and under his guidance High Force quarry in the Whin Sill was visited, specimens of pectolite and zeolites being secured as well as material representative of the gabbroid facies of the sill. The High Force was briefly visited;

then followed tea at the Hotel. Afterwards a call was made at Wynch Bridge to see the alteration of the Whin Sill by lead-vein solutions,[1] associated with fissures feeding small metasomatic deposits in the Single Post Limestone. The dump from war-time exploration of one of these was visited, where blende-chalybite ore, assaying $SiO_2$ 2·9, $Al_2O_3$ 1·3, CaO 5·5, MgO 1·7, Fe 24·6, Zn 19·4, Mn 3·2, S 9·6, BaO trace, $CO_2$ 21·1, F trace (Geological Survey Lab. No. 1091) was examined.

This concluded the tour of the metalliferous mines; typical localities in the fluorspar, fluorspar-galena, galena-blende, and barium zones[2] having been visited.

*Friday, 5th July.*—The last day of the excursion was devoted to a visit to the anhydrite mine and plant of Imperial Chemical Industries at Billingham, south of Durham. Here we were met by Dr. A. E. J. Vickers, Mr. G. S. Gowing, Miss E. Napier, Mr. D. G. A. Whitten, and Mr. E. R. Johnson, and conducted to the mine where the party was taken underground by Mr. G. E. Stewart and Mr. J. T. Owen. The anhydrite deposit worked is a bed 20 feet thick near the middle of the south Durham Permo-Triassic succession having an average dip of 1 in 19 in a direction S. 47° E. The bulk analysis[3] of the mine output over a year is: $CaSO_4$ 90·5, $SiO_2$ 2·1, NaCl 0·006. Detrital minerals present in minor amounts include muscovite, biotite, paragonite, quartz, hornblende, fluorite. The mine is worked from two shafts which reach the anhydrite at a depth of 778 feet below surface. We were conveyed along the impressive main haulage road, 18 feet wide, in a train hauled by an electric locomotive. Workings to the rise and dip were then examined, where features of interest seen included large gypsum crystals in the anhydrite, and an 'intrusion' of red marl and dolomite in the roof of the seam showing evidence of plastic deformation.

The party was entertained to lunch at the works after the visit to the mine; in addition to members of the directorate and staff mentioned above, Mr. A. T. S. Zealley, Dr. M. P. Applebey, and Dr. I. J. Faulkner were also present. There was time for a stroll in the sunshine in the pleasant sports grounds near the works before the next event, which was a talk on sulphate crystallization, illustrated by slides and films, by Mr. J. W. R. Rayner. In this Mr. Rayner gave an account of the

[1] L. R. Wager, Metasomatism in the Whin Sill of the North of England. Part I: Metasomatism by lead vein solutions. Geol. Mag., 1929, vol. 66, pp. 97–110.

[2] K. C. Dunham, The genesis of the north Pennine ore deposits. Quart. Journ. Geol. Soc., London, 1934, vol. 90, pp. 689–720. [M.A. 6–367.]

[3] G. E. Stewart, Billingham mine. Bull. Inst. Mining Metall., 1946, no. 480, pp. 2–4.

work done on the control of the crystal-form of the ammonium sulphate. It had been found that the normal untwinned orthorhombic form was subject to excessive wear, and that it also caused compacting when the sulphate was stored. The product was much more satisfactory when a stout pseudo-hexagonal twinned form predominated.

After a visit to the sulphate-crystallization plant and the cathedral-like storage silo, the party had tea and the excursion came to an end.

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# *Ankerites and chalybites from the northern Pennine orefield and the north-east coalfield.*

(With Plate III.)

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## Introduction

Ankerites from the Northumberland coalfield were first described, with chemical analyses, some ten years ago (Hawkes and Smythe, 1935), when it was found that examples from veins exposed on the coast near Hartley and from sludge from nearby coal-washeries showed a remarkable uniformity in composition. The operations of the collieries concerned cover an area roughly $6 \times 6$ miles, and range from the Beaumont to the High Main Seam. In order to ascertain whether this uniformity is maintained over a wider area, five additional samples of ankerite from veinlets in rocks of Coal Measure age, and one from partings in the Lower Carboniferous Scremerston coal have been examined. The Coal Measure rocks cut by the veinlets have been proved to contain substantial proportions of ferriferous carbonates, while for comparative purposes two examples of rocks of similar age with carbonate but unaccompanied by ankerite veinlets have been investigated. The range in composition of ankerites in the coalfield has proved to be small.

Meanwhile, during the Geological Survey reinvestigation of the northern Pennine orefield, it was found that many of the carbonates formerly described as dolomite are really ankerite, large concentrations of which accompany the galena-blende-fluorite-baryte veins in the form of replacements of limestone or quartz-dolerite. The presence and

[1] By permission of the Director, Geological Survey and Museum.

general range in composition of the northern Pennine ankerites was established by means of refractive index determinations and confirmed by commercial analyses of iron ores of the 'coarse grey' type (Dunham, 1941), but the present account contains the results of the first analyses and determinations on purified material. Here the range in composition is much greater than in the coalfield and the ankerites are accompanied by chalybites of epigenetic origin, samples of which have also been examined.

In the present work, the purification of the samples, the chemical analyses, and the determinations of specific gravity were carried out by Smythe. Optical determinations, petrographical descriptions, and geological notes are by Dunham, except where the last-mentioned were supplied by the donors of specimens. Some of the specimens were of a high order of purity; they were powdered and washed, adventitious lighter matter being removed by floatation in heavy liquids. Others were extremely complex and only yielded pure minerals after laborious fractional separation. The purity of the powders was checked by rigorous optical examination of immersions before analysis.

All the samples contained a little chloride, estimated at 0·04 % in the Stonecroft example (no. 15, below). In most cases ample material was available, but there was insufficient of sample no. 4 for carbon dioxide determination, and the value given in table I is a calculated one. Samples nos. 15 and 17 (table IV) contain respectively 9·48 % and 2·15 % material insoluble in hydrochloric acid. Dr. F. A. Bannister and Dr. G. F. Claringbull have kindly examined the insoluble residues by means of X-rays, and they report as follows:

Residue from sample no. 15 consists mainly of white fragments (quartz and kaolinite) with a few fragments of a buff colour which contain quartz and in addition a phase not so far identified. Residue from sample no. 17 consists mainly of transparent fragments of quartz; goethite and polycrystalline quartz are the constituents of the brown, opaque fragments in the residue.

We are indebted to Mr. W. Anderson and Mr. A. Fowler of the Geological Survey, and to Professor S. E. Hollingworth, who kindly presented the specimens from Easington, Newbiggin, and Carrock Fell respectively. Mr. Anderson also collected the rock from Evenwood. To Mr. H. Berry, of the Fuel Research Coal Survey, Chester, we are grateful for the ankerite from Scremerston. To the Non-ferrous Minerals Development Control, and the Home Ore Department (Iron and Steel Control), of the Ministry of Supply, we tender our thanks for facilities in connexion with their Nenthead and Carricks operations respectively.

## Vein Ankerites from the Coalfield.

The widespread occurrence of ankerite in partings and 'cleat' of coal seams has long been recognized, though the only investigation of the composition of the mineral in the Northumberland-Durham coalfield so far made has been that of the washery sludges mentioned above. The

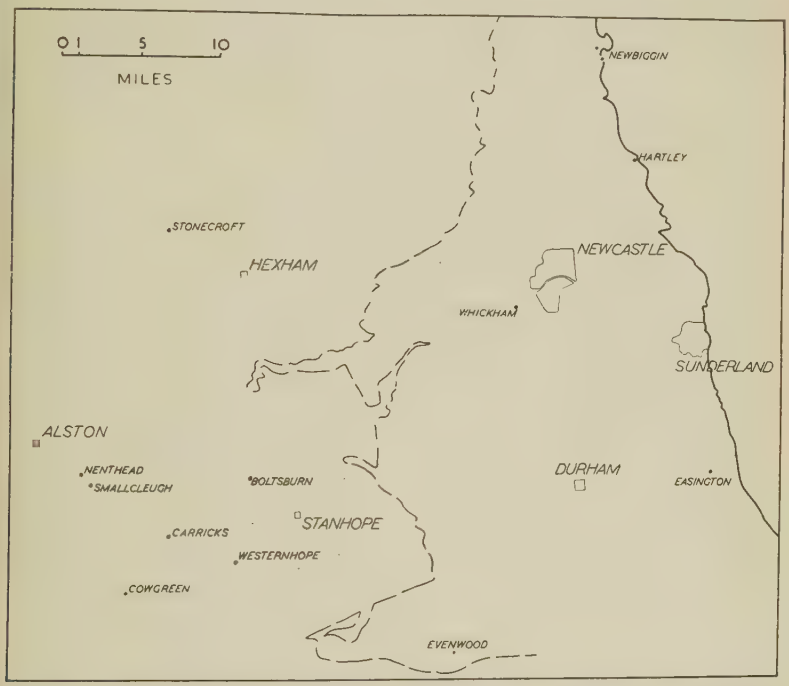


Fig. 1. Sketch-map of the north of England, to show ankerite and chalybite localities to which reference is made. The broken line represents the western margin of the Durham-Northumberland coalfield.

mineral was clearly introduced after the compaction and jointing of the coal, and if further confirmation is needed that the carbonate liquors were from an outside source, it is provided by the occurrence of veins of ankerite in other Coal Measure rocks. Six new examples of vein ankerites are described below.

*Localities and geological relations* (fig. 1).—1. Scremerston Colliery, near Tweedmouth, Northumberland (1-inch map, 1).[1] The sample consisted of plates of the 'white parting' from the cleat of the Scremerston Main coal, of Bernician (Lower Carboniferous) age, which averages 4 feet thick (Fowler 1926, p. 10).

[1] One-inch sheet numbers refer to the New Series maps of the Geological Survey.

2. Newbiggin-by-the-Sea, Northumberland (1-inch map, 10); veinlets from a sandstone of the Upper Group of the Coal Measures, exposed on the foreshore near the south end of the promenade, ¾ mile south-west of the church.

3. Easington Colliery, Co. Durham (1-inch map, 27); up-boring from the shaft; ankerite from vertical veinlet 0·5 mm. wide in 'micaceous sandstone', 10 feet above the Low Main seam (Middle Coal Measures).

4. Easington Colliery, Co. Durham; down-boring from the shaft; thin vein of ankerite in 'clay ironstone', 15 feet below the Hutton seam (Middle Coal Measures).

5. Easington Colliery; undersea boring, 3 miles east of the coast, 1500 feet below sea-level; thin ankerite vein in 'hard, grey, fine-grained sandstone', 127 feet above the Low Main seam.

6. Newbiggin Colliery, Northumberland (1-inch map, 10); ankerite filling a vertical joint found in a boring into 'tough, fine-grained sandstone' above the Brockwell seam (base of Middle Coal Measures).

*Composition.*—In table I the chemical composition, ordinary refractive index, and specific gravity of these ankerites are compared with those from the coast at Hartley, from Hartley Burn, and from Ashington, lettered C, A, and B respectively in Hawkes and Smythe (1935, p. 68). Although not showing the same uniformity as the earlier examples, the range in composition of the new ankerites from the Coal Measures is small, covering, for example, only 4 % MgO. On the other hand, the Scremerston ankerite differs widely from those in the younger rocks.

Table I. Analyses of ankerites from the north-east coalfield.

| | 1. | 2. | 3. | 4. | C. | B. | A. | 5. | 6. |
|---|---|---|---|---|---|---|---|---|---|
| $Al_2O_3$ ... ... | nil | 1·20 | nil | 0·56 | 0·83 | 0·80 | 1·90 | 1·16 | nil |
| $Fe_2O_3$ ... ... | nil | | nil | | | 0·08 | 0·61 | | nil |
| FeO ... ... | 7·84 | 10·30 | 12·20 | 11·54 | 13·54 | 13·04 | 12·53 | 14·72 | 15·68 |
| MnO ... ... | 1·70 | 0·88 | n.d. | 0·50 | 0·75 | 0·75 | 0·61 | n.d. | 0·80 |
| MgO ... ... | 14·91 | 13·95 | 13·74 | 12·72 | 11·45 | 11·02 | 9·98 | 10·65 | 10·94 |
| CaO ... ... | 29·70 | 28·75 | 28·90 | 30·60 | 29·15 | 27·94 | 26·62 | 29·20 | 29·00 |
| $CO_2$ ... ... | 45·10 | 44·50 | 45·16 | 44·10 | 43·50 | 42·40 | 39·65 | 42·66 | 43·40 |
| Insol. ... ... | 0·60 | 0·07 | nil | nil | 0·80 | 3·75 | 7·80 | 1·80 | nil |
| | 99·85 | 99·65 | 100·00 | 100·02 | 100·02 | 99·78 | 99·70 | 100·19 | 99·82 |
| $d\frac{t°}{4°}$ | 2·93 | 2·95 | n.d. | 2·96 | 3·01 | 2·99 | 3·04 | 3·04 | 3·01 |
| $\omega$ ... | 1·692–1·706 | 1·701–1·711 | 1·707–1·713 | 1·709–1·717 | 1·708–1·713 | 1·703–1·717 | 1·703–1·717 | 1·711–1·714 | 1·715–1·717 |
| $FeCO_3$ ... | 12·7 | 16·9 | 19·7 | 18·5 | 22·1 | 22·1 | 22·6 | 24·2 | 25·0 |
| $MnCO_3$ ... ... | 2·8 | 1·4 | — | 0·8 | 1·2 | 1·3 | 1·1 | — | 1·3 |
| $MgCO_3$ ... ... | 31·3 | 29·6 | 28·7 | 26·4 | 24·2 | 24·2 | 23·3 | 22·7 | 22·6 |
| $CaCO_3$ ... ... | 53·2 | 52·1 | 51·6 | 54·3 | 52·5 | 52·4 | 53·0 | 53·1 | 51·1 |
| | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 |
| $FeCO_3.CaCO_3$ ... | 23·6 | 31·4 | 36·7 | 34·4 | 41·1 | 41·2 | 42·0 | 45·1 | 46·6 |
| $MnCO_3.CaCO_3$ ... | 5·2 | 2·7 | — | 1·5 | 2·3 | 2·4 | 2·1 | — | 2·3 |
| $MgCO_3.CaCO_3$ ... | 68·6 | 64·7 | 62·7 | 58·6 | 52·8 | 52·9 | 50·9 | 49·6 | 49·4 |
| $CaCO_3$ ... ... | 2·6 | 1·2 | 0·6 | 5·5 | 3·8 | 3·5 | 5·0 | 5·3 | 1·7 |
| | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 |

## Coal Measure Rocks containing Ferriferous Carbonate.

*Localities and Geological Relations.*—7. Easington Colliery; rock from the down-boring containing vein of ankerite (sample no. 4).

8. Newbiggin Colliery; rock containing vein of ankerite (sample no. 6).

9. Boring 400 yards north-east of Evenwood Colliery, Co. Durham (1-inch map, 32); 'very hard sandstone', 60 feet below the Hutton seam.

10. Easington Colliery; rock from the undersea boring containing vein of ankerite (sample no. 5).

11. Easington Colliery; rock from the up-boring containing vein of ankerite (sample no. 3).

W. Boring at Green's farm, 1½ miles east-south-east of Whickham, Co. Durham (1-inch map, 20); 'limy band in sandstone', 7 inches thick, 11 feet 3 inches below the Hutton Seam. This rock contained the open joint with millerite crystals, described by Anderson and Smythe (1942).

TABLE II. Analyses of ferriferous rocks from the Coal Measures.

| | 7. | 8. | 9. | 10. | 11. | W. |
|---|---|---|---|---|---|---|
| $Al_2O_3$ ... ... / $Fe_2O_3$ ... ... | 0·36 | 0·95 | nil | 2·28 | 3·10 | 1·97 / 0·09 |
| FeO ... ... | 7·77 | 10·20 | 1·66 | 8·65 | 32·92 | 25·41 |
| MnO ... ... | n.d. | n.d. | 0·06 | n.d. | n.d. | 0·10 |
| MgO ... ... | 8·26 | 6·40 | 0·40 | 0·76 | 3·98 | 2·83 |
| CaO ... ... | 18·05 | 18·80 | 1·50 | 0·65 | 7·55 | 4·70 |
| $CO_2$ ... ... | 27·33 | 27·40 | 2·66 | 5·65 | 31·08 | 22·38 |
| $H_2O$ ... ... | 0·35 | 0·05 | trace | 1·30 | 0·50 | 0·60 |
| Insol. ... ... | 37·45 | 35·60 | 93·65 | 80·42 | 21·15 | 42·10 |
| | 99·57 | 99·40 | 99·93 | 99·71 | 100·28 | 100·18 |
| Total carbonate | 60·4 | 61·8 | 6·27 | 14·1 | 76·6 | 55·4 |

*Petrographic descriptions.*—7. (E. 20742)[1] Although described as a fine-grained sandstone in the boring log, the proportion of carbonate in this rock is so high that it should be regarded as a gritty ankerite mudstone. It consists of angular quartz grains averaging 0·1 mm. set in a cryptocrystalline carbonate matrix which is not resolved even at the highest magnifications. The carbonate of the matrix appears to have replaced some of the quartz. Adjacent to the ankerite vein, which contains crystals up to 4 mm. diameter, incipient formation of rhombs in the matrix of the rock is displayed.

8. (E. 20739) The Newbiggin rock is closely similar to that described above. Sharp quartz grains averaging 0·1 mm. are set in a fine-grained carbonate matrix, the ordinary refractive index of the carbonate being approximately 1·715. A little clastic mica is present. There is again a vague suggestion of coarse rhombs in the matrix.

9. (E. 20847) In the Evenwood rock the proportion of carbonate is very much less than in the two preceding rocks. Subangular grains of quartz and shreds of white mica of average length 0·15 mm. make an

[1] Numbers in brackets refer to slides in the Slice Rock collection of the Geological Survey and Museum.

interlocked mosaic in which small patches of fine-grained carbonate occur. A little felspar is present.

10. (E. 20741) Carbonate is a minor constituent in the rock from the undersea boring at Easington, which is a shaly sandstone consisting of rounded quartz grains and shreds of mica averaging 0·06 mm. in a dark streaky matrix. The presence of carbonate here, apart from a few 'pods' seen at high magnification, is not evident under the microscope. Possibly it forms part of the dark matrix.

11. (E. 20740) A normal chalybite mudstone, largely composed of carbonate with average grain-size near 0·005 mm. Opaque minerals including pyrite averaging 0·025 mm. are scattered through the rock and there are rare fragments of quartz and mica. A satisfactory determination of the refractive index of the carbonate has not been obtained, but $\omega$ seems to be near 1·820.

W. (E. 20738) From Whickham comes a gritty chalybite mudstone, with angular quartz grains averaging 0·2 mm. in a chalybite matrix varying from cryptocrystalline to 0·1 mm. in grain size. Shreds of clastic mica and a little oligoclase are present. A few rounded structures in the matrix may represent the remains of ooliths, but these are rare. The ordinary-ray refractive index of the carbonate is 1·830.

*Composition of the rock carbonates.*—In table III the compositions of the rock carbonates, recalculated to 100 %, are compared with those from the veins for which they are the hosts. In the rocks from the down-

Table III. Comparison of vein and rock carbonates.

| | Easington shaft down-boring. | | Newbiggin. | | Evenwood (no vein). |
|---|---|---|---|---|---|
| | 4. Vein. | 7. Rock. | 6. Vein. | 8. Rock. | 9. Rock. |
| $FeCO_3$ ... | 18·5 | 18·0 | 25·0 | 24·1 | 42·7 |
| $MnCO_3$ ... | 0·8 | — | 1·3 | — | 1·4 |
| $MgCO_3$ ... | 26·4 | 28·6 | 22·6 | 21·6 | 13·2 |
| $CaCO_3$ ... | 54·3 | 53·4 | 51·1 | 54·3 | 42·7 |
| Sp. gr. ... | 2·96 | 2·84 | 3·01 | 2·86 | n.d. |
| $\omega$ ... | 1·709 | n.d. | 1·715 | 1·715 | n.d. |

| | Easington undersea boring. | | Easington shaft up-boring. | | Whickham (millerite vein). |
|---|---|---|---|---|---|
| | 5. Vein. | 10. Rock. | 3. Vein. | 11. Rock. | W. Rock. |
| $FeCO_3$ ... | 24·2 | 80·5 | 19·7 | 71·5 | 74·2 |
| $MgCO_3$ ... | 22·7 | 11·3 | 28·7 | 10·9 | 10·7 |
| $CaCO_3$ ... | 53·1 | 8·2 | 51·6 | 17·6 | 15·1 |
| Sp. gr. ... | 3·04 | n.d. | n.d. | n.d. | 3·10 |
| $\omega$ ... | 1·712 | — | 1·710 | 1·820 | 1·830 |

boring at Easington shaft and from Newbiggin, the compositions of the rock and vein carbonates are so close as to justify the assertion that they are of common origin and it seems probable that the rocks have been permeated by carbonate liquors from an extraneous source. Whether a previously existing matrix has been replaced by ankerite, or whether this mineral has been emplaced by replacement of quartz grains is not certain, even though there is clear evidence of attack upon the quartz by the carbonate, for similar relations are normally found in unaltered sedimentary chalybite mudstones. On the other hand, the two other Easington rock carbonates contrast markedly with the vein-ankerites and there is no reason to consider that any genetic relation exists between them. The carbonates in the Easington up-boring and Whickham rocks can readily be matched among the normal chalybite mudstones of the Coal Measures.

### Ankerites from the Orefield.

The northern part of the northern Pennine orefield, lying south-west of the Northumberland–Durham coalfield (fig. 1), between the main Tyne valley and the natural gap of Stainmore, is an area of Lower Carboniferous rocks in which thin limestones are interbedded with shales and sandstones. Intruded into the series is the Whin Sill, a system of sheets of quartz-dolerite at various stratigraphical levels. Ankerite is one, if not the most abundant, of the minerals accompanying the metalliferous veins of the field, from which galena, blende, fluorite, baryte, witherite, and iron ores are produced, particularly where they traverse limestone or dolerite. In limestone, ankerite is in many cases a dominant constituent of the flat deposits, of metasomatic origin, usually extending far beyond the limits of the portions workable for lead, zinc, or iron ores. In the Whin Sill, it appears both in the veins and as a constituent of 'white whin', produced by metasomatism of the dolerite adjacent to them. Ankerite is the chief constituent of the poor-grade 'coarse grey' ore, with which there is reason to think the richer limonitic iron ores of Weardale were formerly diluted for technical purposes (Dunham, 1941). The quantities of ankerite are much greater in the orefield than in the coalfield, and, as a result of metalliferous mining operations, the occurrences are more readily accessible. Nine full analyses of ankerites from the orefield are given below; in addition, one sample has been examined from the Carrock Fell mine in the Lake District, where ankerite is associated with wolframite and scheelite.

*Localities and Geological Relations.*—12. Cowgreen barytes mine, $2\frac{1}{2}$ miles west of Langdon Beck, Co. Durham (1-inch map, 25). Here baryte is being worked from

the Winterhush Vein between walls of Whin Sill and overlying Melmerby Scar Limestone; the orebody varies up to 16 feet wide in the limestone, and contains a mixture of baryte, sugary quartz, and ankerite, with a little galena and blende. In the Whin Sill ankerite is not an important constituent of the vein, but it is abundantly present in the altered dolerite. The sample was taken from the coarse tailings of the dressing plant.

13. Carricks ironstone mine, Wearhead, Co. Durham (1-inch map, 25). The deposits worked consist of replacement flats in the Great Limestone, related to weak NE.–SW. and E.–W. veins. Beneath the oxidation zone, the primary minerals are chalybite, ankerite, and quartz, with minor quantities of galena and fluorite. Within the oxidation zone, both ankerite and chalybite are replaced by limonite (this term being used here to mean hydrated ferric oxide, with subsidiary manganese oxides). The ankerite of sample no. 13 is particularly associated with a belt of NNW.–SSE. cross veins lying west of the main orebodies; it would normally be classified in the field as fine-grained, iron-stained dolomite. The typical ankerites associated with the orebodies are represented by samples nos. 19–21, below.

14. Carrock Fell wolfram mine, 7 miles NE. of Keswick, Cumberland (1-inch map, 23). Here a small complex of wolframite-quartz veins occurs, the wall-rocks being greisen and gabbro. Associated minerals include molybdenite, scheelite, arsenopyrite, pyrite, and chalcopyrite; carbonates, recorded as calcite and dolomite, occur according to Hitchen (1934, p. 191) as the latest phase of the mineralization, associated with sulphides. The ankerite sample examined was from Harding Vein, where a new level has recently (1942–3) been driven; it was separated from a specimen in which calcite (with $\omega$ 1·664) and quartz were present.

15. Stonecroft mine, 2 miles WNW. of Fourstones, near Hexham, Northumberland (1-inch map, 13). An abandoned lead mine, Stonecroft worked galena-baryte veins between Whin Sill walls. Pale brown coarse ankerite is abundantly present on the extensive dumps, forming according to an estimate based on the magnesia-content of representative samples taken during the Geological Survey investigation, at least 20 % of their total mineral contents. Other minerals present in the veins included quartz, blende, witherite, and pyrite; Sir Arthur Russell informs us that he has found harmotome here. The ankerite sample was collected from the coarse dump near Stonecroft winding shaft.

16. Smallcleugh mine, half a mile south of Nenthead, Cumberland (1-inch map, 25). One of the most extensive metasomatic galena deposits of the northern Pennines, the Smallcleugh flats are replacements of the lowest 10–15 feet of the Great Limestone in a horst bounded to the south-west and north-east by Smallcleugh and Handsome Mea Great cross veins respectively. An excellent description of the deposit, with a block diagram, has been given by Wallace (1861, pp. 135–6, plate XIV), who has estimated that not less than five million cubic feet of limestone have undergone decomposition here. Although the workings have long been abandoned, it was found possible to examine parts of them in 1931. Ankerite forms coarse white streaks, roughly parallel to the bedding of the limestone; it is also abundantly present, with quartz, in the fine-grained hard matrix of the deposit. Other minerals in the flats included blende, pyrite, fluorite, chalybite, and calcite, in roughly that order of abundance. The sulphides were deposited either contemporaneously with, or later than, the ankerite. The sample examined was derived from one of the white streaks in the deposit. Recently the mine dumps have been treated by flotation for recovery of their zinc-content. Separations of ankerite were made from a representative sample of the feed to the mill;

it is estimated that ankerite forms approximately 35 % of the total mineral contents.

17. Westernhope 'New' mine, 2¾ miles SSE. of Westgate in Weardale, Co. Durham (1-inch map, 25). Metasomatized Great Limestone, related to the Ash Hill and Westernhope Great galena-fluorite veins is exposed in an opencut on the east bank of Ash Cleugh, the eastern headwater of Westernhope Burn. Like most of the occurrences in Weardale, the ankerite forms a medium-grained rock composed of interlocking idioblastic rhombs, with individual crystals up to 2 mm. long. The sample was separated from this rock, which also contains some chalybite.

18. Carricks ironstone mine; underground boring to no. 4 Cross Vein, south of Dawson's Vein, no. 4, 9 feet. The sample consisted of white rhombs from a cavity in highly ankeritized limestone.

19. Boltsburn mine, Rookhope, Co. Durham (1-inch map, 25). The metasomatic flats in the Great Limestone associated with Boltsburn Vein, worked for galena from 1898 to 1931, contained fluorite, chalybite, ankerite, quartz, and calcite, with minor quantities of blende, pyrite, and chalcopyrite. Between the workable portions of the flats and the vein there was generally a belt of 'rider' (described by Carruthers as 'close-grained, ferruginous and dolomitic limestone', 1923, p. 11, footnote) varying from a few feet up to 20 feet wide. D. F. Hewett (1928, p. 836) has described the flat at Boltsburn as 'a tabular mass of dolomitized limestone breccia' and has stated that 'the dolomite is uniformly light gray in color and coarsely crystalline'. Microscopic investigation of specimens collected before the mine was flooded has now shown that the supposed dolomite is in fact ankerite with a high proportion of $FeCO_3$. The sample represents the 'rider' between the vein and the workable flat after removal of chalybite, which was also present.

An estimate of the quantitative importance of ankerite at Boltsburn may be gained from the fact that nearly 40 % of the crude ore, of which a little over half a million tons were mined between 1901 and 1931, consisted of ankerite.[1] Great quantities of the mineral remain in the unworked portions of the deposit.

Carbonaceous material is present in the Boltsburn sample, presumably remaining from the limestone which has been replaced. Determinations on the mineral concentrate gave C 0·6 %; H 0·8 % and on the dried residue of material insoluble in hydrochloric acid, C 4·2 %, H 5·9 %. Some of the hydrogen may be from hydrous minerals.

20. Carricks ironstone mine; white rhombs from a cavity in the metasomatized Great Limestone associated with Lowe's Vein. The sample was pure and free from chalybite.

21. Carricks ironstone mine; Lowe's Vein West boring no. 1, 190 feet. The core specimen was chosen as representing the typical carbonate iron ore of this mine; it consisted of a mixture of coarse, pale grey, interlocking rhombs of ankerite, with yellow chalybite in streaks and irregular masses. The sample is a concentrate of ankerite separated from this mixture; a concentrate of chalybite was also prepared and analysed (no. 22, below). A small quantity of chalybite remains in the ankerite concentrate, but it is considered not to exceed 3 %.

*Composition.*—The analyses in table IV indicate a wide range in composition among the northern Pennine ankerites, with corresponding ranges in refractive index and specific gravity. The Cowgreen mineral,

[1] This estimate is based on recent samplings of the tailings heaps.

TABLE IV. Analyses of ankerites from the northern Pennine orefield and the Lake district.

| | 12. | 13. | 14. | 15. | 16. |
|---|---|---|---|---|---|
| $Al_2O_3$ ... ... / $Fe_2O_3$ ... ... | 0·63 | 3·01 | 0·69 | 0·69 | 0·60 |
| FeO ... ... | 3·30 | 5·20 | 7·50 | 13·90 | 13·72 |
| MnO ... ... | 1·18 | 1·39 | 3·44 | 0·42 | 1·90 |
| MgO ... ... | 18·71 | 14·60 | 14·26 | 8·52 | 10·33 |
| CaO ... ... | 29·85 | 31·20 | 29·05 | 27·20 | 29·20 |
| $CO_2$ ... ... | 45·72 | 44·23 | 44·71 | 39·45 | 43·33 |
| Insol. ... ... | 0·25 | 0·30 | trace | 9·48 | 0·55 |
| | 99·64 | 99·93 | 99·65 | 99·66 | 99·63 |
| $d\frac{t^\circ}{4^\circ}$ ... ... | 2·86 | 2·91 | 2·96 | 2·95 | 3·00 |
| $\omega$ ... ... ... | 1·685–1·689 | 1·690–1·695 | 1·694–1·700 | 1·709–1·711 | 1·702–1·725 |
| $\epsilon$ ... ... ... | 1·507 | n.d. | n.d. | 1·523 | n.d. |
| $FeCO_3$ ... ... | 5·3 | 8·7 | 12·1 | 25·0 | 22·4 |
| $MnCO_3$ ... ... | 1·9 | 2·3 | 5·6 | 0·8 | 3·1 |
| $MgCO_3$ ... ... | 39·3 | 31·5 | 30·1 | 19·9 | 21·8 |
| $CaCO_3$ ... ... | 53·5 | 57·5 | 52·2 | 54·3 | 52·7 |
| | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 |
| $FeCO_3.CaCO_3$ ... | 9·9 | 16·2 | 22·8 | 46·6 | 41·2 |
| $MnCO_3.CaCO_3$ ... | 3·6 | 4·3 | 10·5 | 1·4 | 5·8 |
| $MgCO_3.CaCO_3$ ... | 85·9 | 68·9 | 65·8 | 43·6 | 47·1 |
| $CaCO_3$. ... ... | 0·6 | 10·6 | 0·9 | 8·4 | 5·9 |
| | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 |

| | 17. | 18. | 19. | 20. | 21. |
|---|---|---|---|---|---|
| $Al_2O_3$ ... ... / $Fe_2O_3$ ... ... | 0·73 | 0·66 | nil | 2·13 | 1·96 / 0·57 |
| FeO ... ... | 14·92 | 20·20 | 20·88 | 23·30 | 22·61 |
| MnO ... ... | 2·53 | 2·38 | 1·25 | n.d. | 2·24 |
| MgO ... ... | 8·01 | 6·24 | 5·34 | 4·88 | 3·01 |
| CaO ... ... | 29·25 | 27·80 | 27·85 | 27·62 | 28·30 |
| $CO_2$ ... ... | 42·22 | 42·07 | 40·82 | 41·00 | 40·91 |
| Insol. ... ... | 2·15 | 0·35 | 3·40 | 0·67 | 0·83 |
| | 99·81 | 99·70 | 99·54 | 99·60 | 100·43 |
| $d\frac{t^\circ}{4^\circ}$ ... ... | 3·03 | 3·08 | 3·07 | 3·05 | 3·11 |
| $\omega$ ... ... | 1·716–1·722 | 1·720–1·729 | 1·721–1·727 | 1·722–1·733 | 1·727–1·734 |
| $\epsilon$ ... ... ... | 1·529 | n.d. | n.d. | n.d. | 1·536 |
| $FeCO_3$ ... ... | 24·8 | 32·9 | 34·9 | 38·7 | 37·6 |
| $MnCO_3$ ... ... | 4·2 | 3·9 | 2·1 | — | 3·7 |
| $MgCO_3$ ... ... | 17·2 | 13·2 | 11·5 | 10·5 | 6·5 |
| $CaCO_3$ ... ... | 53·8 | 50·0 | 51·5 | 50·8 | 52·2 |
| | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 |
| $FeCO_3.CaCO_3$ ... | 46·2 | 61·3 | 65·0 | 72·2 | 70·1 |
| $MnCO_3.CaCO_3$ ... | 7·8 | 7·3 | 3·9 | — | 6·9 |
| $MgCO_3.CaCO_3$ ... | 37·6 | 28·8 | 25·2 | 23·0 | 14·2 |
| $CaCO_3$ ... ... | 8·4 | 2·6 | 5·9 | 4·8 | 8·8 |
| | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 |

with only 5·3 % $FeCO_3$, is not far removed from the dolomite end of the series, while the white crystals from Carricks mine, with 38·7 % $FeCO_3$, contain 72·2 % ferrodolomite. Refractive index measurements showed some variation of ordinary-ray index within individual samples. In some instances this was as little as 0·002, and only one sample, that from Smallcleugh, showed a greater range than 0·011. In some instances this variation is due to zoning, such as the Carricks mine crystals (no. 20) display. At Cowgreen two distinct ankerites were found; that of the analysed sample (no. 12), with $\omega$ 1·685–1·689, and another with $\omega$ 1·712. The latter was carefully removed in the purification process, but it did not prove possible to obtain a sufficiently clean concentrate for analysis. Ankerites intermediate in composition between the two were not present. At Smallcleugh, on the other hand, evidence was obtained of a range with many intermediate stages present, from $\omega$ 1·682 up to $\omega$ 1·728. The analysed sample, separated in Sonstadt's solution (mercuric iodide in potassium iodide) was freed from the lighter dolomitic ankerite, and the full range represented by this sample is $\omega$ 1·702 to 1·725, with very rare grains reaching 1·728. The light crop from the separation (not analysed) contained ankerites ranging down to $\omega$ 1·682.

In an examination of typical mill-feed to the flotation plant at Nenthead, derived from the dumps at Smallcleugh and other adjacent mines, the same range in refractive indices was noted. In separations it was found that the heaviest fraction, sinking in Sonstadt's solution, contained ankerite with $\omega$ 1·710 to 1·723, together with blende, galena, pyrite, and fluorite. Middlings from this separation consisted of ankerite with $\omega$ 1·695 to 1·718, the bulk lying between 1·700 and 1·710. Floats carried ankerite ranging down to $\omega$ 1·682, with calcite, quartz, and micaceous minerals. Repeated separations failed to produce samples of ankerite sufficiently pure to warrant analysis.

### Chalybites from the Orefield.

Three samples of chalybite from Carricks mine have been isolated from spathic ores in which it is the most important constituent. Sample 22 is from Lowe's Vein West boring no. 1 at 190 feet from the same core-specimen as the ankerite concentrate, no. 21. Sample 23 comes from the same boring, at 242 feet; sample 24 from Lowe's Vein West boring no. 11 at 155 feet. In each case the chalybite is present in the metasomatized limestone in the form of irregular yellow streaks, associated with more or less ankerite. Zoning was not found when the powders were examined microscopically, but in the case of sample 22 a small quantity of ankerite,

present as minute inclusions of low refractive index, was noted. In samples 23 and 24, however, the purity of the powders is such as to preclude the possibility that appreciable amounts of free ankerite are present.

TABLE V. Analyses of chalybites from Carricks mine, Weardale, Co. Durham.

| | 22. | 23. | 24. |
|---|---|---|---|
| $Al_2O_3$ ... | 0·55 | 2·83 | 0·40 |
| $Fe_2O_3$ ... | 0·94 | | |
| FeO ... | 47·20 | 52·00 | 51·87 |
| MnO ... | 3·45 | n.d. | 3·17 |
| MgO ... | 2·86 | 2·78 | 2·50 |
| CaO ... | 4·80 | 3·62 | 3·60 |
| $CO_2$ ... | 37·74 | 38·21 | 38·28 |
| Insol. ... | 2·65 | trace | trace |
| | 100·19 | 99·44 | 99·82 |
| $d_{4^0}^{t^0}$ ... | 3·58 | 3·73 | 3·77 |
| $\omega$ ... | 1·838 | 1·839 | 1·841 |
| $\epsilon$ ... | n.d. | n.d. | 1·611 |
| $FeCO_3$ ... | 79·1 | 87·2 | 83·3 |
| $MnCO_3$ ... | 5·8 | — | 5·1 |
| $MgCO_3$ ... | 6·2 | 6·1 | 5·2 |
| $CaCO_3$ ... | 8·9 | 6·7 | 6·4 |
| | 100·0 | 100·0 | 100·0 |

## MINERALOGICAL DISCUSSION.

*Chemical composition.*—The whole suite of sixteen new and three earlier analyses (Hawkes and Smythe, 1935) of ankerite from north-eastern England provides a progressive series in which the contents of $MgCO_3$ range, in small steps, from 39·3 to 6·5 %, while those of $FeCO_3$ vary from 5·3 to 38·7 %. The analyses confirm the tendency, often noted, for the approximate constancy in content of $CaCO_3$ which led Doelter (1912, p. 371) to the conclusion that the mineral consists of isomorphous mixtures of dolomite and ferrodolomite. It is clear from older analyses, as well as from the new data here presented, that this is too simple a view of the series. The present analyses show contents of manganese carbonate varying between 0·8 and 5·6 %, while calcium carbonate is present in every sample in excess of that required to satisfy dolomite, ferrodolomite, and mangandolomite, varying in amount unsystematically up to 10·6 %. As shown by the data summarized by R. G. Wayland (1942, p. 616), the ionic radius of iron is nearer to that of manganese than are the radii of magnesium or calcium; it is thus most probable that the manganese is present as a substitution of iron, but

it may be noted that Wayland's work also suggests extensive miscibility between $MnCO_3$ and $CaCO_3$. A convenient picture of the ankerite series may be constructed in terms of *ferromangandolomite* $(Fe,Mn)CO_3.CaCO_3$, dolomite, and calcite (fig. 2).

No natural occurrence of pure ferrodolomite or magnesia-free ferromangandolomite has ever been recorded, and the samples from Carricks

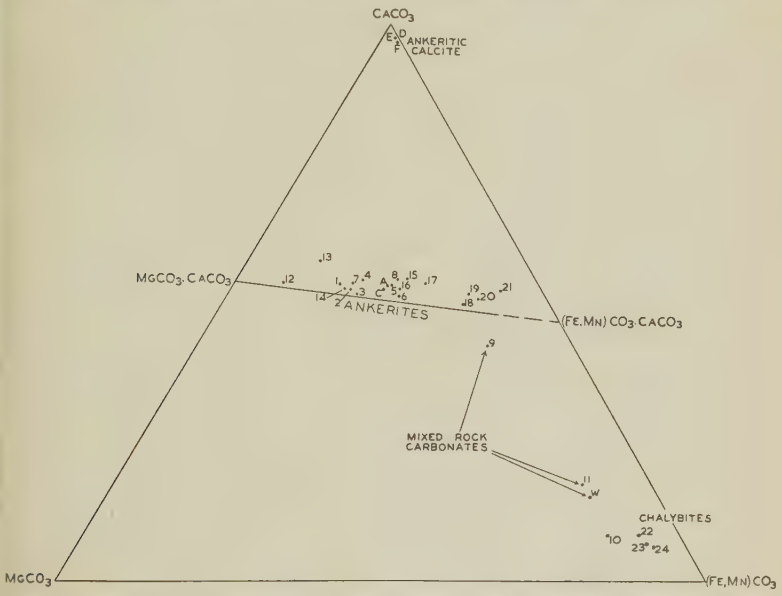


Fig. 2. Diagram to illustrate the compositions of the ankerites, chalybites, and ankeritic calcites in terms of $CaCO_3$, $MgCO_3$, $(Fe,Mn)CO_3$.

and Boltsburn mines here described represent, with one exception,[1] the nearest approach to this end of the supposed series so far recorded. The ferromangandolomite-contents, disregarding sample 21, are 68·6 (18) and 68·9 % (19), while in sample 20, in which owing to paucity of material manganese was not determined, there was 72·2 % ferrodolomite. In view of the association with chalybite of contemporaneous or nearly contemporaneous origin in these occurrences it is possible that the absence of carbonates nearer in composition to ferrodolomite may have a real significance, and that the isomorphous series ends between 65 and

[1] For which E. S. Larsen and H. Berman (Bull. U.S. Geol. Surv., 1934, no. 848, p. 88) give the following data: $CaCO_3$ 48·3, $MgCO_3$ 11·3, $FeCO_3$ 37·9, $MnCO_3$ 2·5 %; $\omega$ 1·749, $\epsilon$ 1·547.

75 % $(Fe,Mn)CO_3.CaCO_3$. The Smallcleugh sample provides evidence of continuity from dolomite to this stage, and it is considered that the other samples, in which the range of composition is small, represent the results of local equilibria. The Evenwood rock carbonate (no. 9) perhaps supports the contention of limited miscibility. Its composition suggests a mixture of ankerite and chalybite, though unfortunately the material is so fine-grained that unequivocal microscopical confirmation of this has not been obtained. The occurrence without associated ankerite veins makes it unlikely that the carbonate cement has been subjected to later replacement by ankerite. The composition may be expressed as follows: $FeCO_3$ 13·0; $FeCO_3.CaCO_3$ 55·4; $MnCO_3.CaCO_3$ 2·7; $MgCO_3.CaCO_3$ 28·9 %. The ankerite portion, assuming that the chalybite is pure $FeCO_3$, would contain 66·7 % ferromangandolomite.

It is tentatively suggested that ankerite may be defined as an isomorphous series containing the carbonates of magnesium, calcium, iron, and manganese not containing more than approximately 70 % ferrodolomite, in which a limited proportion of manganese carbonate may be present,[1] and in which calcium carbonate in excess of that required to form dolomite, ferrodolomite, and mangandolomite may occur in amounts up to 20 %.[2] The series is not linked either with the ankeritic calcites or the chalybites through homogeneous intermediate compounds. The structure of the ankerites, the manner in which substitution takes place, and the way in which the 'excess' $CaCO_3$ is accommodated remain to be investigated by X-ray methods.

Of the three analyses of chalybites from Carricks mine, two contain $MgCO_3$ and $CaCO_3$ in the proportions required to form dolomite, with a slight excess of $MgCO_3$ in one case. A third analysis (no. 22) of the sample known to carry a little adventitious ankerite can be expressed as containing dolomite plus 3·9 % ankerite with 70 % ferrodolomite (table VI). It is remarkable, therefore, that these three analyses can be interpreted in terms of chalybite and non-ferriferous dolomite. The small quantities of manganese in these samples are assumed to occur as substitutions of iron in the chalybite.

The rock carbonates from the Coal Measures are not capable of explanation in terms of chalybite, rhodochrosite, and dolomite. One of them (no. 10) contains excess of $MgCO_3$, pointing to a member of the

[1] An ankerite described by Wayland (1942, p. 628) from Butte, Montana, contains 6·9 % $MnCO_3$.

[2] See H. W. Foote and W. M. Bradley, Amer. Journ. Sci., 1914, ser. 4, vol. 37, p. 343.

TABLE VI. Recalculated compositions of chalybites.

| | 22. | 23. | 24. | 10. | 11. | W. |
|---|---|---|---|---|---|---|
| $(Fe,Mn)CO_3$ ... | 83·3 | 87·2 | 88·4 | 80·5 | 71·9 | 74·1 |
| $FeCO_3.CaCO_3$* ... | 3·1 | — | — | — | — | — |
| $MgCO_3.CaCO_3$*... | 0·8 | — | — | — | — | — |
| $MgCO_3.CaCO_3$ ... | 12·8 | 12·4 | 11·6 | 15·1 | 23·1 | 23·4 |
| $MgCO_3$ ... | — | 0·4 | — | 4·4 | — | — |
| $CaCO_3$ ... | — | — | — | — | 5·0 | 2·5 |
| | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 |

* In the proportions 3 dolomite : 7 ferrodolomite.

chalybite-magnesite series, stages in which have been named by T. Crook (1919, p. 75); there is, however, no evidence as to the stage which is represented. The other two (no. 11 and W) contain a sufficient excess of $CaCO_3$ and could be calculated as mixtures of ankerite and chalybite; but in the absence of satisfactory optical evidence as to the homogeneity of the carbonates it is not proposed to discuss this further.

*Refractive index.*—The determinations recorded in tables I, III, and IV were made by the immersion method, using yellow monochromatic illumination. Values for the extraordinary-ray index quoted were obtained on grains oriented on an improvised microscope goniometer. It was not considered justifiable to attempt determinations of $\epsilon$ except in the case of samples where the range of $\omega$ was known to be small.

The refractive index measurements indicate that none of the analysed ankerites is completely homogeneous in the sense that all the material present has constant indices; each sample represents a smaller or greater part of the isomorphous group. In fig. 3 the values for $\omega$ are plotted against dolomite-content. In many samples showing a range in refractive indices the bulk of the grains in the immersions examined were found to correspond to a much more restricted range; for example, in no. 2 $\omega$ ranges from 1·701 to 1·711, but the great majority of the grains showed $\omega$ 1·706. Where predominant values could reasonably be determined these are shown on the diagram. Comparing the ranges of $\omega$ determined for the present material with the line joining the accepted value for pure dolomite (1·680) and that deduced from the literature by Hawkes and Smythe (1935, p. 72) for pure ferrodolomite (1·765) all the values are low and would appear to be lower than substitution by manganese and the presence of 'excess' $CaCO_3$ can fully explain.

It will be evident that, from a practical point of view, determination of refractive index gives only a very approximate guide to composition in this complex system. W. E. Ford (1917) has shown that refractive indices, as well as specific gravities of the minerals of the calcite group

calculated from the percentages of the simple carbonates corresponds reasonably accurately with the determined values. Confirmation of this was obtained in the case of the ankerites and chalybites described here.

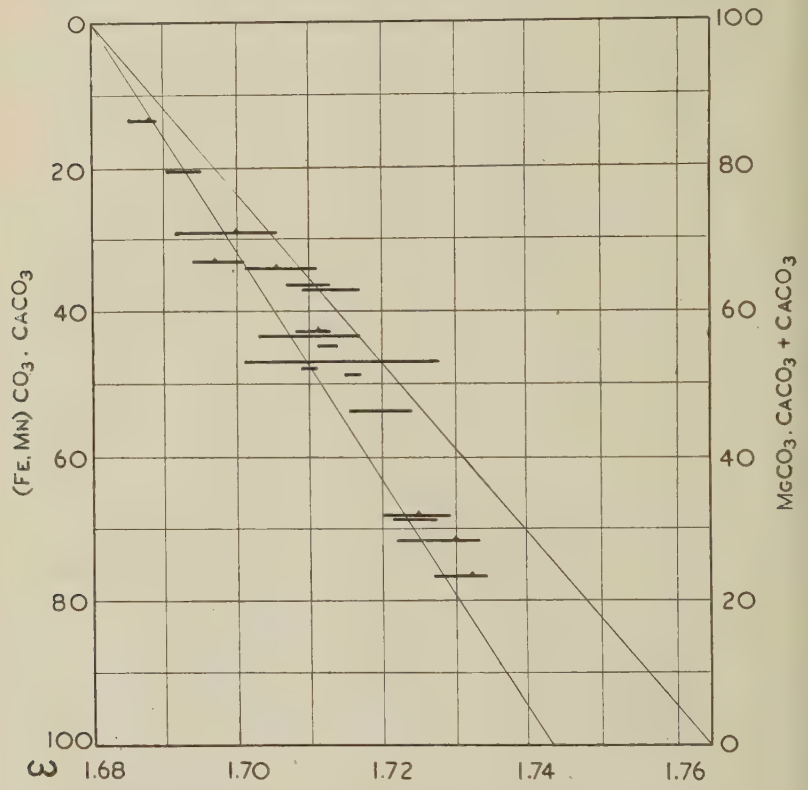


Fig. 3. Ordinary-ray refractive indices of ankerites, plotted against dolomite plus 'excess' calcite and ferromangandolomite. The cross-mark indicates the probable mean index where this can be determined.

*Specific gravity.*—This property gives a slightly more accurate guide to composition than refractive index, but even so it only serves to define certain limits as possibilities. In fig. 4 the relation between specific gravity and composition for the ankerites here described is shown; values to which small corrections for impurities (on the assumption that these had a specific gravity of 2·65) had been applied were used in the construction of this diagram. The substitution of manganese for iron has only a very small effect upon the specific gravity.

*Textural relations.*—In all parts of the orefield, ankerite appears to have been the earliest, or one of the earliest, products of the mineralization process. In the replacement deposits limestone was converted into a rock composed of interlocked sharp rhombs of ankerite before the deposition of sulphides. In examples like Boltsburn the selvedge of ankeritized limestone alongside the vein was unfavourable to further replacement, and galena-fluorite deposits were formed only where the solutions were able to break through this selvedge to reach fresh limestone beyond. Deposition of ankerite continued, however, and was partly

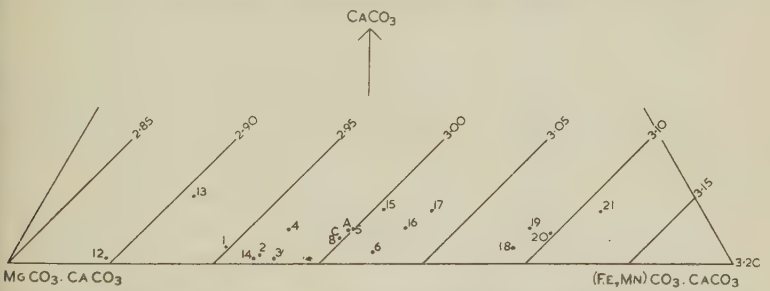


Fig. 4. Specific gravities of ankerites, after correction for impurities, in relation to composition.

contemporaneous with the sulphides. The Smallcleugh material provides evidence that deposition of ankerite commenced at the dolomite end of the series, and became more ferriferous and less magnesian at later stages; the cloudy cores of the crystals here range between $\omega$ 1·682 and 1·700; the outer zones, clearer of inclusions, are also of higher refractive index. By the use of the staining method devised by Hallimond (1925, p. 39), in which a chip of rock is treated with hydrogen peroxide before sectioning, it was found that ankerite could be preferentially stained, the more ferriferous zones taking a darker stain. Applied to material from Middlehope mine, Weardale, this showed dolomitic inner zones and ferriferous outer zones in ankerite from replacements of the Great Limestone (pl. III, fig. 1). On the other hand, sections of the core from Carricks mine, from which samples 21 and 22 were extracted, failed to show zoning in the ankerite, confirming the small range of composition indicated by refractive index measurements. Of the two ankerites at Cowgreen mine that with the lower refractive index (no. 12) crystallized first.

There is equally definite evidence that in the metasomatized limestone chalybite crystallized later than ankerite, wrapping itself about

the ankerite rhombs and in places cutting through them in tiny veinlets. The process of formation of the carbonates may thus be envisaged as starting with dolomite and proceeding towards the ankerite with 65–75 % ferrodolomite. This was reached if adequate supplies of iron were available, but after this more ferriferous ankerite was not formed; instead, chalybite with dolomite in solid solution was deposited.

It is interesting to note that whereas in the case of the low-temperature Pennine mineralization ankerite is an early mineral, in the Carrock Fell paragenesis, where minerals considered to be of high-temperature origin are present, the ankerite is a late-stage product.

*Oxidation of ankerite and chalybite.*—Within the 'oxidation zone', above the groundwater table, waters of surface origin carrying dissolved oxygen and carbon dioxide act upon the carbonates. In the orefield the depth of this zone varies from zero adjacent to the valley-bottoms to a maximum of about 300 feet beneath the hills. The product of oxidation of both ankerite and chalybite is a mixture of hydrous ferric and manganese oxides; crystalline goethite is rare. Chalybite is more responsive to oxidation than ankerite, as might be expected, and at most of the Weardale ironstone mines specimens of dense limonite (after chalybite) containing sharp rhombs of little-altered ankerite can be picked up. At a more advanced stage, however, ankerite is itself attacked, and preferential oxidation shows up the ferriferous zones in much the same way as the staining process mentioned above. The alteration of ankerite to limonite involves the release of calcium and magnesium bicarbonates; the substantially lower magnesia- and lime-contents of the oxidized 'brown haematite' ores as compared with the primary spathic ores (Dunham, 1941, pp. 7, 8) strongly suggest that these constituents are carried away. No doubt they are, however, redeposited elsewhere:

TABLE VII. *Comparison of primary and oxidized iron ores, Carricks mine.*[1]

| | 'Fine steel grey' (Chalybite). | 'Coarse grey' (Ankerite). | 'Brown haematite' (Limonite). |
|---|---|---|---|
| $FeCO_3$ ... | 73·4 | 31·2 | 0·0 |
| $MnCO_3$ ... | 7·0 | 4·6 | 0·0 |
| $MgCO_3$ ... | 3·8 | 10·0 | 0·3 |
| $CaCO_3$ ... | 8·5 | 28·0 | 1·3 |
| $(Fe,Mn)_2O_3.xH_2O$ ... | 0·0 | 0·0 | 81·4 |
| $FeS_2$ ... | 1·3 | 0·3 | 0·0 |
| $SiO_2$ ... | 5·6 | 22·1 | 16·1 |
| | 99·6 | 96·2 | 99·1 |

[1] Recalculated from analyses by L. C. W. Birkett, 1940, quoted in Dunham, 1941, table III, nos. 2–4.

possibly the dolomitic ankerite found as an iron-stained, fine-grained 'dolomitization' zone along the cross veins at Carricks mine (sample 13) is the product of such a process.

*Origin of the carbonates.*—Ankerite is widespread throughout the northern part of the northern Pennine orefield, north of Stainmore.[1] Chalybite, in quantity, is of more restricted range, the principal deposits being in Upper Weardale. It is a striking fact that the most ferriferous ankerite is always associated with chalybite, and that its refractive index $\omega$ does not exceed 1·734. In relation to the zonal arrangement of minerals in the orefield (Dunham, 1934) the iron-rich areas are found in the inner, fluorite-galena zone east of the Burtreeford disturbance. In the outer zones more magnesian ankerites occur.

In the southern part of the northern Pennines, south of Stainmore, covering the west Yorkshire dales, on the other hand, ankerite is very rare, though otherwise similar suites of metalliferous minerals occur. The most important difference between the northern and southern parts of the orefield is the presence in one and the absence in the other of the Whin Sill. L. R. Wager (1929, p. 105) has made the interesting suggestion that the lead vein solutions in the northern area derived their iron through the metasomatism of the Whin Sill. The alteration process adjacent to the veins consisted of the conversion of ferromagnesian minerals into carbonates and felspars into micaceous minerals. The chemical data already available (Finlayson, 1910; Wager, 1929; Smythe, 1930) show that iron is abstracted in the process, together with, in certain cases but not in others, magnesia. Possibly, therefore, the metasomatism of the Whin Sill is sufficient to explain the abundant ankerite and chalybite of the northern area. It should be made clear, however, that the hydrothermal solutions responsible for the Pennine mineralization were not themselves the product of the Whin Sill; this dolerite has its own suite of hydrothermal products, and ankerite is not one of them.

It is tempting to regard the ankerites of the coalfield as products of the same widespread mineralization as those of the orefield. Baryte and witherite deposits are, indeed, worked in the Coal Measures, and there can be little doubt that these represent the outer zone of the Pennine mineralization; but they are not accompanied by ankerite. A small galena-calcite vein, described by H. Louis (1903, p. 128) from the shale and sandstone roof of the Maudlin Seam at Wearmouth Colliery,

[1] Refractive index measurements on crystals from numerous localities are given in the forthcoming Geological Survey Memoir on the orefield.

Sunderland, had carbonate mineralization associated with it in the coal itself; the composition of the carbonate, in spite of the author's unsupported conclusion to the contrary, strongly suggests ankerite. Recalculated from the analysis quoted, it contains ferrodolomite 50, dolomite 38, calcite 12 %; or if the zinc present is assumed to be in the sulphide state, then the ferrodolomite figure is slightly increased in proportion. Possibly some of the ankerite in the Coal Measures came from the same hydrothermal source as that in the orefield; but as yet there is no evidence as to the origin of the widespread partings of this mineral in the coals.

## Summary of Conclusions.

1. Sixteen new analyses of ankerite from the Northumberland-Durham coalfield and the northern part of the northern Pennine orefield, taken in conjunction with three earlier analyses (Hawkes and Smythe, 1935), provide evidence of a range of solid solutions from dolomite up to 65–75 % ferromangandolomite; calcium carbonate in excess of that required for dolomite and ferromangandolomite is always present. Ordinary ray refractive indices $\omega$ range from 1·682 to 1·734.

2. Since the most ferriferous ankerite of the series occurs in intimate association with chalybite it is suggested that the ankerite series ends at 65–75 % ferrodolomite.

3. Chalybites from the orefield contain dolomite, but not ferrodolomite, in solid solution.

4. Crystallization of ankerite from hydrothermal solutions proceeded from dolomite towards ferrodolomite; after the limit of solid solution had been reached, chalybite with dolomite in solid solution appeared instead of ankerite.

5. The distribution of ankerite in the northern Pennines is consistent with Wager's view (1929) that the iron was derived through the metasomatism by lead vein solutions of the Whin Sill; it is suggested that magnesia was supplied to the solutions from the same source.

6. In two rocks from the Coal Measures contiguous with ankerite veinlets ankeritization is demonstrated; in three other Coal Measure rocks carbonate cements, presumably of sedimentary origin, consist of chalybite possibly mixed with ankerite.

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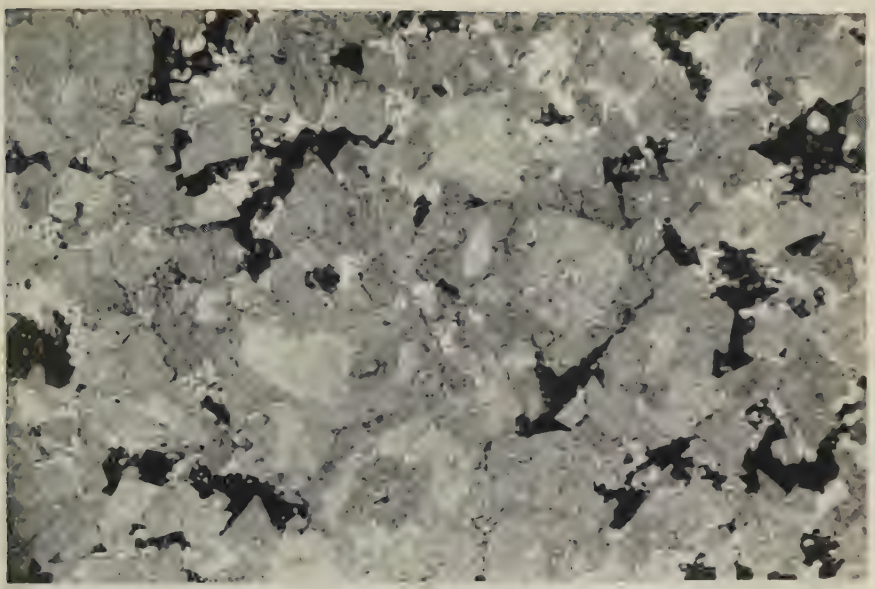
## Explanation of Plate III.

Photomicrographs of thin sections of Great Limestone after staining with KOH and $H_2O_2$. Black and dark grey areas are chalybite. The tint of the ankerite varies according to its iron-content.

Fig. 1. Middlehope mine, 1¼ miles north of Westgate in Weardale, Co. Durham. (Section E. 18903A; Geological Survey Photograph M. 2295.) To show dolomitic cores in ferriferous ankerite. In some instances the cores preserve the form of fossil fragments. Late chalybite is present. Ordinary light, × 15.

Fig. 2. Carricks ironstone mine, no. 2 borehole, Lowe's Vein West, at 66 feet, Weardale, Co. Durham. (Section E. 19999A, Geological Survey Photograph M. 2296.) To show a gash lined with zoned ankerite rhombs and filled with chalybite. Ordinary light, × 15.



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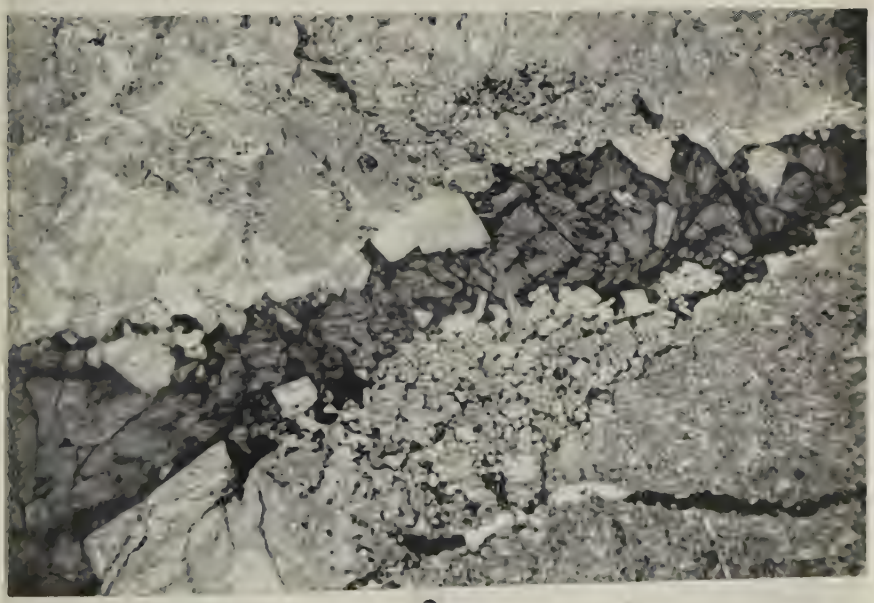

2

J. A. Smythe and K. C. Dunham, Ankerite and Chalybite.

# *The occurrence of artificial kalsilite and allied potassium aluminium silicates in blast-furnace linings.*

(With Plate IV.)

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[Communicated by Dr. F. A. Bannister; read January 23, 1947.]

## I. Introduction.

THE contour and dimensions of a typical blast furnace are shown in fig. 1. The shell of the furnace consists of riveted steel plates, inside which is a lining of firebricks varying in thickness about 2-3½ feet. Molten iron collects in the crucible or hearth at the bottom of the furnace and is periodically run off through a hole in the side of the furnace known as the tap-hole. The hearth is lined with firebrick both around the sides and along the floor, the total thickness of brickwork below the hearth in fig. 1 being 3 feet 9 inches.

A blast furnace after completely relining with firebrick may be in continuous operation for several years during which period upwards of a million tons of iron may be made, necessitating the charging of some 2–3 million tons of iron ore, coke, and limestone through the bell at the top of the furnace. When the furnace is in blast the firebrick lining is exposed to the abrading action of the descending burden and the cutting effect of the ascending blast charged with fine particles of coke and ore. The brickwork is also chemically corroded, being exposed to alkali vapours, lime-bearing slags, and the disintegrating action of carbon monoxide which dissociates, depositing carbon within the brick structure.

It has long been the practice of the British Refractories Research Association to examine blown-out furnace linings with a view to determining which zones in the furnace are subjected to the most severe wear. Samples of the slagged brickwork are also removed for laboratory examination.

A common feature of the brickwork in the middle and lower stack region is that the hot face of the lining is often vitrified due to alkali

vapours reacting with the alumina and silica in the brickwork, forming alkali alumino-silicates. A typical thin section cut inwards from the working face often reveals crystals of orthorhombic $KAlSiO_4$, while farther towards the brick mullite and leucite can be detected. More

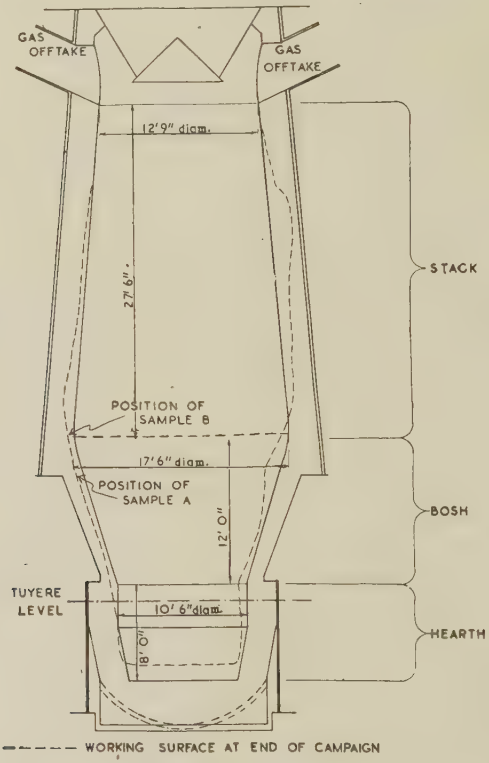


Fig. 1. Section of Kettering no. 3 blast furnace, showing extent of wear of firebrick lining and position of specimens A and B.

recently various samples have been subjected to X-ray examination by the Debye-Scherrer powder method when the presence of kalsilite has been confirmed by comparing the results with the X-ray powder data given by F. A. Bannister.[1] A. H. Jay (see Appendix) of the United Steel Companies has also independently verified the presence of kalsilite in samples taken from blast-furnace stacks. These minerals, kalsilite, orthorhombic $KAlSiO_4$, and leucite, would appear to be readily formed

[1] F. A. Bannister and M. H. Hey, Min. Mag., 1942, vol. 26, p. 218.

by the action of alkali vapours on firebricks under the conditions prevailing in the blast furnace, but until quite recently they have only been detected associated with glass or admixed with furnace burden adhering to the surface of the brickwork and they could not be obtained in anything approaching a state of purity.

## II. The hearth of the Kettering no. 3 furnace.

A few months ago an opportunity was given to one of the authors by the Kettering Iron and Coal Co. to examine their no. 3 furnace. This

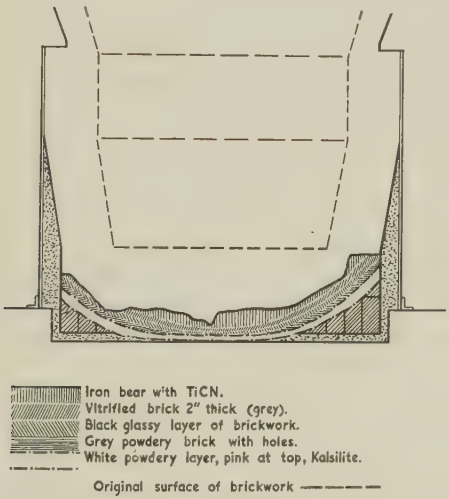
Iron bear with TiCN.
Vitrified brick 2" thick (grey).
Black glassy layer of brickwork.
Grey powdery brick with holes.
White powdery layer, pink at top, Kalsilite.
Original surface of brickwork

Fig. 2. Section of hearth of blast furnace, showing zoning of deposits.

furnace, the dimensions of which are given in fig. 1, had been in blast for six years and had made some 250,000 tons of iron. The stack of the furnace had been lined with bricks of the following percentage composition: $SiO_2$ 55·6, $Al_2O_3$ 40·3, $Fe_2O_3$ 0·84, MgO 0·27, CaO 0·28, $Na_2O$ 0·37, $K_2O$ 2·02, while the percentage analysis of the bosh and hearth brickwork was as follows: $SiO_2$ 53·5, $Al_2O_3$ 42·4, $Fe_2O_3$ 2·6, MgO 0·5, CaO 0·4, $Na_2O$ trace, $K_2O$ 0·1. The contours of the brickwork before and after the furnace campaign are shown in fig. 1. Samples of brickwork were taken at intervals all down the stack, and vitrification of the working face of the lining consequent upon alkali attack was a noticeable feature of some of these samples. Before excavating the hearth it was first necessary to remove a quantity of frozen iron which had collected due to the floor of

the hearth having been eroded to a dish-shaped contour extending below the tap-hole level. The next procedure was to remove the brickwork remaining below this mass of frozen iron. Under the combined influences of pressure, temperature, and reducing conditions it is common to find that this brickwork has vitrified to a porcelain-like monolithic mass, but with the furnace in question a most unusual condition was observed. A vertical section cut through the hearth showed the presence of a number of well-defined zones which are depicted in fig. 2. The uppermost zone extending to a depth of 2 inches consisted of vitrified brickwork; this was followed by a second zone having a black glassy appearance, also extending for a depth of 2 inches. This zone was found to consist of glass containing numerous cordierite crystals. The zone below this was some 5 inches deep and consisted of a white, soft, powdery material with a strong smell of cyanide. The upper portion of this zone was coloured pink and at the centre of the hearth the white material had displaced the layer of coke and tar ramming on which the hearth brickwork was built. Below this white zone near to the wall of the hearth the original brickwork could be identified, the bricks were intensely vitrified but the joints between individual bricks were clearly defined. The curved nature of these zones and their sharp demarcation were, no doubt, imposed by the temperature gradients in the hearth, the isotherms following a similar curvature.

### III. Examination of the white deposit.

The material was found to consist largely of kalsilite, the chief impurity being potassium carbonate. In spite of the strong smell of cyanide pervading the samples, analysis showed that the actual cyanide content was below 0·25 %. This was, however, sufficient to give colour reactions with the iron oxide, and the grey-white material gave an intense green coloration on adding hydrochloric acid. Various samples were taken across the hearth; sample I gave the following percentage analysis: $SiO_2$ 32·1, $TiO_2$ 0·70, $Al_2O_3$ 29·1, $Fe_2O_3$ 1·5, MgO 0·27, CaO 0·50, $Na_2O$ 2·2, $K_2O$ 29·1, loss on ignition 4·2 ($CO_2$ 3·5), cyanides trace. The percentage analysis of a second sample was: $SiO_2$ 30·0, $TiO_2$ 0·35, $Al_2O_3$ 26·4, $Fe_2O_3$ 1·4, MgO 0·12, CaO 0·45, $Na_2O$ 2·7, $K_2O$ 30·3, loss on ignition 7·2 ($CO_2$ 6·3). These analyses indicate that sample I consisted of about 90 % kalsilite, 5·7 % potassium carbonate, and 4·3 % excess alumina, ferric oxide, lime, and magnesia. Similar figures for sample II are: 81 % kalsilite, 12·2 % potassium carbonate, and 6·8 % excess silica, alumina, ferric oxide, &c.

Specific gravity determinations were made on a number of samples which were first purified from potassium carbonate by floatation in a benzene-bromoform solution of density 2·4. The heavier material had densities ranging from 2·60 to 2·61. A thin section was cut from a piece of lumpy material from sample I. The crystals were very small, the largest being only about 0·07 mm. long. Under a 2-mm. oil-immersion objective good almost uniaxial negative interference-figures were obtained from several crystals. Refractive indices obtained by the Becke method were $\omega$ 1·537, $\epsilon$ 1·530 ($\pm$0·002). None of the crystals possessed a hexagonal outline: the majority were rectangular in shape as may be seen from pl. IV, fig. 3. The crystals were elongated parallel to the slow direction (i.e. had positive elongation), indicating a tabular habit. No suggestion of any cleavages was apparent in any of the crystals.

X-ray powder photographs of the two samples were also taken using a 9-cm. camera and filtered cobalt radiation (pl. IV, figs. 8 and 9). The lattice spacings recorded in table I agree remarkably well with those previously recorded by F. A. Bannister for the natural mineral kalsilite found in rocks from Mafuru, Uganda. Observed and calculated values for $\sin^2\theta$, where $\theta$ is the Bragg angle, are also listed in table I, the calculated values being obtained from the lattice dimensions of natural kalsilite as given by F. A. Bannister, viz.: $a$ 5·17, $c$ 8·67 kX. The relative intensities of the reflections given by samples I and II are also listed and it will be observed that there are differences in the intensities of certain of the reflections. X-ray examination of samples containing kalsilite previously found in the stacks of two blast furnaces at two other plants gave photographs in which the relative intensities as well as the positions of the reflections agreed with those of sample I rather than sample II. It should be emphasized that these intensity differences are not accompanied by any noticeable line movement indicative of solid solution effects, but it would appear that differences occur in the reflecting power of the atom-bearing planes in the various samples. Differences in chemical analysis between samples I and II do not appear to account satisfactorily for these intensity variations, as, for example, the higher percentage of potassium carbonate in sample II. It will also be observed that the percentages of ferric oxide, lime, and soda are of a similar order in the two samples. The intensity values reported for natural kalsilite generally agree with those obtained for sample I rather than for sample II.

TABLE I. X-ray data for kalsilite. For the natural mineral from F. A. Bannister, 1942. Bravais indices omitting the third index.

| Relative intensities. Sample I. | Sample II. | $d$ (kX) Artificial mineral. | $d$ (kX) Natural mineral. | *hkl*. | $\sin^2\theta$ Artificial mineral. | $\sin^2\theta$ Calculated for natural mineral. |
|---|---|---|---|---|---|---|
| m | vw | 4·33 | 4·35 | 002 | 0·0426 | 0·0425 |
| s | s | 3·96 | 3·97 | 101 | 0·0511 | 0·0505 |
| vs | s | 3·10 | 3·11 | 102 | 0·0832 | 0·0824 |
| s | vs | 2·569 | 2·590 | 110 | 0·1212 | 0·1195 |
| m | m | 2·454 | 2·470 | 111 | 0·1326 | 0·1302 |
| m | vw | 2·415 | 2·428 | 103 | 0·1369 | 0·1355 |
| m | m | 2·208 | 2·218 | 112 | 0·1638 | 0·1602 |
| s | m | 2·161 | 2·163 | 004 | 0·1711 | 0·1701 |
| w | w | 1·979 | 1·984 | 202 | 0·2040 | 0·2019 |
| vw | vw | 1·948 | 1·955 | 104 | 0·2104 | 0·2099 |
| w | w | 1·921 | 1·926 | 113 | 0·2167 | 0·2152 |
| w | w | 1·764 | 1·770 | 203 | 0·2566 | 0·2550 |
| m | m | 1·654 | 1·660 | 114 or 211 | 0·2921 | 0·2895, 0·2896 |
| m | w | 1·615 | 1·620 | 105 | 0·3062 | 0·3056 |
| s | m | 1·570 | 1·576 | 212 | 0·3239 | 0·3214 |
| m | vw | 1·552 | 1·556 | 204 | 0·3314 | 0·3294 |
| s | s | 1·485 | 1·490 | 300 | 0·3624 | 0·3586 |
| m | w | 1·456 | 1·460 | 213 | 0·3770 | 0·3746 |
| vw | vw | 1·443 | n.d. | 006 | 0·3838 | 0·3827 |
| m | w | 1·369 | 1·375 | 106 | 0·4261 | 0·4225 |
| w | w | 1·330 | 1·335 | 214 | 0·4512 | 0·4490 |
| m | m | 1·286 | 1·294 | 220 | 0·4826 | 0·4781 |
| m | w | 1·261 | 1·264 | 116 | 0·5022 | 0·5022 |
| m | w | 1·226 | 1·231 | 311 or 304 | 0·5317 | 0·5286 |
| m | w | 1·209 | 1·212 | 215 | 0·5462 | 0·5446 |
| m | m | 1·189 | 1·194 | 312 | 0·5651 | 0·5604 |
| w | w | 1·138 | 1·141 | 313 | 0·6169 | 0·6136 |
| vw | vw | 1·108 | 1·111 | 401 or 224 | 0·6512 | 0·6481, 0·6482 |
| w | w | 1·081 | 1·085 | 402, 207, or 008 | 0·6836 | 0·6801, 0·6802, 0·6803 |
| w | vw | 1·054 | 1·055 | 108 | 0·7181 | 0·7201 |
| w | vw | 1·038 | 1·036 | 225 | 0·7419 | 0·7437 |
| m | w | 1·007 | 1·011 | 315 | 0·7854 | 0·7837 |
| vw | vw | 1·000 | 1·000 | 322 or 118 | 0·7991 | 0·7994, 0·7998 |

## IV. THE OCCURRENCE OF POTASSIUM-ALUMINIUM SILICATES IN BLAST-FURNACE SAMPLES.

N. L. Bowen[1] recognizes two distinct crystal phases of $KAlSiO_4$. The low-temperature phase is hexagonal, isomorphous with nepheline, uniaxial negative, with $\omega$ 1·532, $\epsilon$ 1·527. Natural kaliophilite from Monte Somma may be identical with this low-temperature phase, and S. J. Thugutt[2] claims to have prepared artificial kaliophilite at 208–211° C. identical with the natural mineral. N. L. Bowen also recognizes a high-

[1] N. L. Bowen, Amer. Journ. Sci., 1917, ser. 4, vol. 43, p. 115. [M.A. 1–167.]

[2] S. J. Thugutt, Arch. Min. Tow. Nauk. Warszaw., 1937, vol. 13, p. 112. [M.A. 7–146.]

temperature form of kaliophilite which is orthorhombic, optically negative, and twins similar to aragonite, with $\alpha$ 1·528, $\gamma$ 1·536. More recently, M. H. Hey (Bannister and Hey, loc. cit., 1942) has succeeded in preparing an orthorhombic form of $KAlSiO_4$ twinned like aragonite. Bowen states that both the hexagonal and orthorhombic forms of $KAlSiO_4$ can be obtained at low temperatures, but the hexagonal form inverts to the orthorhombic form in the neighbourhood of 1540° C.

Good crystals of orthorhombic $KAlSiO_4$ can often be observed in the slagged face of brick samples from blast furnaces. Pl. IV, fig. 4, is a thin section cut from slagged brickwork from the stack at position A (text-fig. 1) (sample A). The X-ray pattern showed the presence of $KAlSiO_4$ free from leucite (fig. 11). The crystals were not entirely homogeneous, a few were uniaxial negative, basal sections were hexagons while other sections were square or rectangular in outline. Other crystals appeared to be biaxial positive with a very small axial angle. These crystals showed interpenetration twinning of the aragonite type. The refractive indices were $\alpha$ 1·534, $\gamma$ 1·540. In contrast with kalsilite the rectangular sections had negative elongation, there was also a suggestion of a cleavage parallel to *c*.

A sample obtained from the stack of the Kettering furnace at position B (fig. 1) had a vitrified working face and a thin section revealed well-developed crystals (fig. 5). Some of these crystals showed complex polysynthetic twinning sometimes in more than one direction. They were biaxial positive with refractive indices $\alpha$ 1·528, $\gamma$ 1·533. The crystals tended to a prismatic or lath form, the laths having negative elongation. Away from the edge of the section the crystals progressively altered, the twinning became less pronounced and finally disappeared, while the birefringence increased until crystals similar to those shown in fig. 4 were encountered. Crystals similar to these have been noticed previously and an illustration is given in fig. 6 where they occurred in a sample obtained from a blast-furnace stove. X-ray photographs of sample B showed the presence both of orthorhombic $KAlSiO_4$ and leucite (fig. 12).

With regard to the number of crystalline forms of $KAlSiO_4$ and their relative stability the following observations can be made from a study of blast-furnace samples.

(1) Optically uniaxial negative crystals of orthorhombic $KAlSiO_4$ free from twinning have been observed in samples which have been exposed for long periods at temperatures around 1000–1100° C. X-ray powder

photographs have shown that these crystals are orthorhombic (pseudo-hexagonal).

(2) Optically biaxial positive crystals twinned like aragonite have also been observed, and in addition biaxial positive crystals with complicated twinning like leucite have been noticed and these crystals have been associated with leucite. Such crystals have been formed in close proximity to the uniaxial negative form of orthorhombic $KAlSiO_4$ and give the same X-ray photograph.

(3) A massive deposit of kalsilite contaminated with 5–10 % of potassium carbonate has been found in the blast-furnace hearth some 4 or 5 inches below molten iron. The temperature of formation of this kalsilite must therefore be in the region 700–1100° C.

(4) Kalsilite has been detected in stack samples from blast furnaces where the temperature range would again be 700–1100° C.

It is not the purpose of this paper to explain how the deposit of kalsilite originated below the hearth, but it is of some importance with regard to the stability of the $KAlSiO_4$ minerals to suggest the mechanism of their synthesis in the furnace. It has long been appreciated that alkalis are present in the blast furnace, and the flue dust passing over with the gases has sometimes been treated for the recovery of alkalis. The alkali content of the ore supplying the Kettering furnace is not known, but assuming it to be as low as 0·1 % this represents the introduction of no less than 750 tons of alkali into the furnace during its six years' campaign. It is probable that the potash continuously accumulates inside the furnace, being vaporized at the tuyere level and condensing again when it meets the cooler materials at the top of the furnace. The management have occasionally noticed the presence of molten potassium cyanide floating on the iron as it is tapped from the furnace. It is probable that the alkali is initially vaporized as cyanide or chloride, but at certain positions in the furnace these salts are decomposed by free iron oxide or water vapour to the corresponding oxides which then slag the brickwork. The potassium carbonate found with the kalsilite probably originated from the hydrolysis of the cyanide since the hearth was finally cooled by means of water-sprays after all possible iron had been tapped from the furnace. The alumina and silica must have been derived from the fire-bricks and it is interesting in this connexion to observe that the molecular ratio of alumina to silica is almost 1:2. This being the case it should be possible to synthesize kalsilite in the laboratory without resorting to hydrothermal methods at high pressures since the pressure in the blast furnace is only a few centimetres

of mercury higher than atmospheric. Accordingly, a number of experiments were conducted in the laboratory to try and establish the relationship between kalsilite and kaliophilite.

## V. The synthesis of potassium aluminium silicates in the laboratory.

(*a*) *The synthesis of kaliophilite.*—The experiments were mainly carried out with the object of synthesizing kalsilite. A china-clay was chosen as a source of silica and alumina in which the molecular proportion of these constituents was 2:1 and other impurities were low. The percentage analysis of the china-clay was as follows: $SiO_2$ 46·90, $Al_2O_3$ 39·08, $Fe_2O_3$ 0·66, MgO 0·02, CaO 0·05, $Na_2O$ 0·14, $K_2O$ 0·42, loss on ignition 12·72. Four mixtures were made up of the following compositions:

(1) One molecular proportion of china-clay and one molecular proportion of potassium carbonate.
(2) As no. (1) with the addition of 5 % of $Fe_2O_3$.
(3) As no. (1) with the addition of 5 % of kalsilite.
(4) As no. (1) but with twice the amount of potassium carbonate.

The materials were placed in a furnace and heated for various periods at temperatures of 900° C. (60 hours), 1100° C. (5 hours), and 1300° C. (5 hours). A stream of nitrogen saturated with water vapour at 25° C. was maintained through the furnace. X-ray photographs of the materials gave the following information. When heated to 900° C. all specimens gave the same X-ray pattern (pl. IV, fig. 7). This pattern was distinct from that given by the kalsilite or orthorhombic $KAlSiO_4$ from sample A in the blast furnace. Examination of the X-ray photographs suggests that this low-temperature form of $KAlSiO_4$ is hexagonal and it is probably identical with the low-temperature form previously described by N. L. Bowen. It can be indexed according to the data for natural kaliophilite given by F. A. Bannister, *a* 27, *c* 8·51 kX.

When heated to 1100° C. nos. (1) and (3) specimens still gave the same pattern as at 900° C., no. (2) specimen gave mainly the same pattern as at 900° C. but there was a pattern developing identical with that obtained from the blast-furnace sample A. Specimen (4) gave a pattern which was identical with that obtained from sample A (fig. 11). This is probably the high-temperature orthorhombic form of $KAlSiO_4$ described by N. L. Bowen. This form of $KAlSiO_4$ appears to be the stable modification at high temperatures, the inversion temperature being between

900 and 1100° C. When heated to 1300° C. all specimens gave patterns similar to that of sample A, but in specimens nos. (1) and (3) additional lines corresponding to leucite could be detected, suggesting that alkali was being volatilized from these two specimens.

F. A. Bannister has kindly supplied a sample of an orthorhombic form of $KAlSiO_4$ showing twinning of the aragonite type, and X-ray examination showed this to be identical with blast-furnace sample A and the high-temperature orthorhombic form prepared by us. The optical properties of this orthorhombic form appear, however, to vary in certain samples, e.g. in sample A the crystals appear to be pseudo-hexagonal and twinning is not marked. Other samples show twinning of the aragonite type, and finally there are well-developed crystals as in sample B with polysynthetic twinning similiar to microcline or leucite. These latter samples appear to have a lower birefringence, lower refractive indices, and a larger axial angle than the untwinned types. There would appear to be some disagreement with regard to the optical sign of the orthorhombic form, which we find to be biaxial positive in the crystals exhibiting complicated twinning (pl. IV, figs. 5 and 6). These variations might be accounted for by partial loss of potash due to volatilization; it appears significant that orthorhombic $KAlSiO_4$ showing polysynthetic twinning is associated with leucite.

The lattice spacings for the low-temperature and orthorhombic forms of $KAlSiO_4$ are given in table II and the X-ray photographs in figs. 7 and 11.

(*b*) *The synthesis of kalsilite.*—Since kalsilite was obtained in none of the above experiments, small specimens of kalsilite from the furnace hearth contaminated with the potassium carbonate associated with this deposit were heated at 900°, 1100°, and 1300° C. respectively. X-ray examination showed that the specimen was unchanged after heating to 900° and 1100° C., but the specimen fired to 1300° C. had begun to decompose to orthorhombic $KAlSiO_4$, giving an additional X-ray pattern identical with that obtained from blast-furnace sample A. This alteration at 1300° C. requires time to complete and intermediate specimens were obtained showing the kalsilite pattern together with a pattern similar to that obtained on heating the china-clay and potassium carbonate mixes to 900° C., indicating that with this deposit the alteration from kalsilite to orthorhombic $KAlSiO_4$ was by way of this low-temperature hexagonal form. These experiments suggested that the upper temperature limit for synthesizing kalsilite would be below 1300° C.

TABLE II. Main space-lattice reflections of the high-temperature orthorhombic $KAlSiO_4$ (fig. 11) and of the low-temperature hexagonal form, kaliophilite (fig. 7).

| High-temperature orthorhombic form. | | Low-temperature hexagonal form, kaliophilite. | |
|---|---|---|---|
| Intensity. | *d* (kX). | Intensity. | *d* (kX). |
| w | 6·21 | w | 4·50 |
| m | 5·75 | m | 4·26 |
| w | 4·51 | s | 3·10 |
| m | 4·26 | fs | 2·61 |
| w | 3·88 | m | 2·22 |
| fs | 3·56 | m | 2·14 |
| m | 3·41 | vw | 1·65 |
| w | 3·30 | w | 1·58 |
| s | 3·10 | vw | 1·55 |
| fs | 2·79 | w | 1·50 |
| m | 2·67 | w* | 1·25 |
| fs | 2·61 | vw* | 1·19 |
| m | 2·23 | | |
| m | 2·13 | | |
| vw | 2·10 | | |
| w | 2·07 | | |
| w | 1·76 | | |
| m | 1·72 | | |
| w | 1·58 | | |
| m | 1·48 | | |
| w | 1·425 | | |
| m | 1·25 | | |
| w | 1·23 | | |
| m | 1·20 | | |

* Diffuse lines on the photograph.

Since small additions of ferric oxide had failed to produce kalsilite when added to the appropriate china-clay and potassium carbonate mixes, additions of lime as calcium carbonate, metallic iron, and alumina were next tried, but without success. The chemical analyses of kalsilite both from natural sources and from the blast-furnace hearth showed the presence also of soda and magnesia; accordingly experiments were made with an addition of sodium carbonate equivalent to 3 % of $Na_2O$. On heating this mixture to 850° C. in a furnace through which a stream of nitrogen saturated with water vapour was passed a specimen was obtained which gave a good X-ray photograph of kalsilite free from kaliophilite or unreacted materials (pl. IV, fig. 10). Further experiments elucidated that an atmosphere saturated at 25° C. with water vapour was not necessary. Rather surprisingly, if the china-clay was substituted by powdered firebrick similar to that used in the hearth of the blast furnace the reaction proceeded more readily and at 850° C. the mixture was converted to kalsilite in a few hours.

A series of experiments was finally carried out to determine more closely the stability range of this mineral. The following mixes were made up for these experiments:

(1) Powdered firebrick (analysis given earlier in the paper) with the addition of the appropriate amount of potassium carbonate plus 0·5 % $Na_2O$ (as carbonate) based as a weight percentage on the composition $KAlSiO_4$.
(2) Similar to mix (1) with the addition of sodium carbonate equivalent to 1·0 % $Na_2O$.
(3) Similar to mix (1) with the addition of 1·5 % $Na_2O$.
(4) As mix (1) with the addition of 2·0 % $Na_2O$.
(5) As mix (1) with the addition of 5·0 % $Na_2O$.
(6) A mix consisting of equimolecular proportions of the two carbonates to give the theoretical composition $(Na,K)AlSiO_4$.

These mixes were then heated at temperatures of 650°, 750°, 850°, 1000°, 1100°, and 1200° C. At 650° C. the reaction was slow and unchanged brick was still present at the end of 5 hours. At all other temperatures kalsilite was obtained with the specimens containing additions of 2 % and 5 % soda, but increase in soda content caused line movement in the kalsilite pattern. At temperatures of 650°, 750°, and 850° C. the specimens containing 0·5, 1·0, and 1·5 % additions of soda gave the low-temperature hexagonal kaliophilite, while at 1000°, 1100°, and 1200° C. the specimens containing 0·5 and 1·0 % additions gave the high-temperature orthorhombic $KAlSiO_4$. At 1100° and 1200° C. mix (3) containing 1·5 % addition of soda gave a photograph indicating a mixture of kalsilite and orthorhombic $KAlSiO_4$. Mix (6) containing equimolecular proportions of sodium and potassium gave two solid phases; variations in the space-lattice indicated that these were a sodium-rich kalsilite together with a potassium-rich nepheline. It would appear therefore that a small percentage of sodium is essential for kalsilite to crystallize out, the minimum amount being equivalent to more than 1·5 % and less than 2·0 % $Na_2O$ based on the theoretical amount of kalsilite which can be formed. In this connexion it is interesting to note that the analysis of natural kalsilite given by M. H. Hey contained 2 % of $Na_2O$ if the impurities are ignored, while the kalsilite from the blast-furnace hearth was associated with 2·5–3·0 % of $Na_2O$. It is also probable that this minimum amount of sodium varies with the temperature of formation.

The decomposition at 1300° C. of a specimen prepared from the

kalsilite deposit found in the blast furnace suggests that kalsilite becomes unstable at some temperature below its melting-point. Experiments undertaken to determine the range of stability showed that kalsilite containing 1·5 % of soda was decomposed at 1300° C.; with 2·0 % of soda the temperature of decomposition was between 1300° and 1350° C.; and with 5 % soda kalsilite was stable at 1500° C. From changes in the space-lattice as revealed by X-ray photographs, the limit of replacement of potassium by sodium at 1100° C. is reached with the addition of 5 % $Na_2O$. Although changes in lattice spacings were noted with kalsilite containing varying amounts of sodium no difference in relative intensities comparable with those given by the blast-furnace samples were observed.

## VI. General conclusions.

Our experiments and observations would indicate the existence of three minerals having the chemical composition $KAlSiO_4$.

The low-temperature modification is hexagonal and is probably similar to natural kaliophilite. It is formed when the correct proportions of silica, alumina, and potash are heated below 900° C.

The high-temperature modification is orthorhombic and is synthesized by heating the correct proportions of silica, alumina, and potash at temperatures over 1000° C. This orthorhombic form of $KAlSiO_4$ has been found in blast-furnace linings. Occasionally crystals are almost uniaxial and free from twinning, other crystals are biaxial positive and exhibit twinning like aragonite, while still other crystals are biaxial positive and show polysynthetic twinning sometimes in two directions. It is suggested that these differences are due to some loss of potash by volatilization, as the form showing polysynthetic twinning is usually associated with leucite.

The third mineral, kalsilite, can only be formed in the presence of sodium. With 1·5 % addition of $Na_2O$ to the correct mixture of silica, alumina, and potash, some kalsilite is formed at 1100° and 1200° C. With 2 % and 5 % $Na_2O$ additions kalsilite is readily formed on heating to temperatures above 650° C. The upper temperature limit of stability is also dependent on the sodium content; with 1·5 % $Na_2O$, kalsilite is decomposed to orthorhombic $KAlSiO_4$ below 1300° C., with 2 % of $Na_2O$ the temperature of decomposition is between 1300° and 1350° C., and with 5 % of $Na_2O$ it is above 1500° C.

*Acknowledgements.*—We should like to acknowledge the help we have received and to express our thanks to: Mr. G. H. Johnson and Mr. T. Hodson of the Kettering Iron and Coal Co., Ltd. for giving us all facilities

to examine their blast furnace and collect samples; Dr. F. A. Bannister of the British Museum for the interest he has shown in the research; Mr. A. T. Green, Director of the British Refractories Research Association for permission to publish this paper, Miss F. Ball for her assistance in the laboratory, and Mr. W. Hugill for taking the photographs.

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Explanation of Plate IV.

Artificial potassium aluminium silicates. Figs. 3–6, photomicrographs of thin sections. Figs. 7–12, X-ray powder photographs taken in a 9-cm. camera with filtered cobalt radiation, 1·787 kX.

Fig. 3. Artificial kalsilite excavated from below the hearth (text-fig. 2), sample 1. ×200.

Fig. 4. Thin section cut from the slagged brickwork in the stack (position A, text-fig. 1), sample A, showing crystals of orthorhombic $KAlSiO_4$. ×100.

Fig. 5. Thin section from vitrified working face of the stack (position B, text-fig. 1), sample B, showing orthorhombic $KAlSiO_4$ and leucite. ×100.

Fig. 6. Orthorhombic $KAlSiO_4$, showing polysynthetic twinning, from a blast-furnace stove.

Fig. 7. Artificial kaliophilite prepared in the laboratory, p. 83.

Fig. 8. Artificial kalsilite, sample 1 (fig. 3), excavated from the hearth of the Kettering no. 3 furnace; chemical analysis, p. 78, X-ray data, p. 80.

Fig. 9. Artificial kalsilite, sample 2, excavated from hearth of Kettering no. 3 furnace; chemical analysis, p. 78; X-ray data, p. 80.

Fig. 10. Artificial kalsilite prepared in the laboratory, p. 85.

Fig. 11. Orthorhombic $KAlSiO_4$, sample A, from the stack at position A (cf. figs. 1 and 4).

Fig. 12. Orthorhombic $KAlSiO_4$ and leucite, sample B, from the stack at position B (cf. figs. 1 and 5).

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## Appendix.

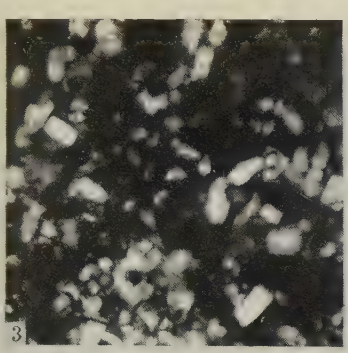
### *X-ray reflections of kalsilite* ($K_2O.Al_2O_3.2SiO_2$).

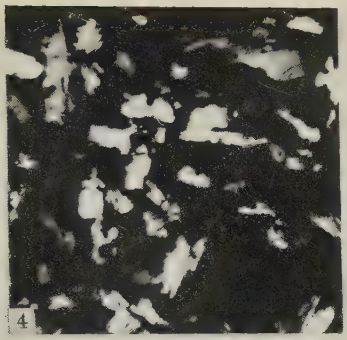
By A. H. Jay,[1] Ph.D., F.Inst.P and K. W. Andrews, D.Phil.

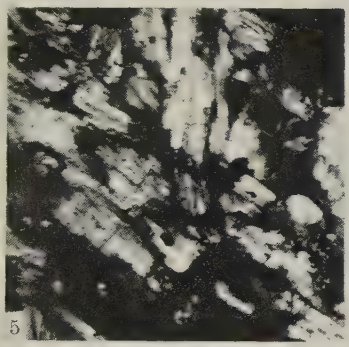
The United Steel Companies Limited, Research and Development Department, Stocksbridge, near Sheffield.

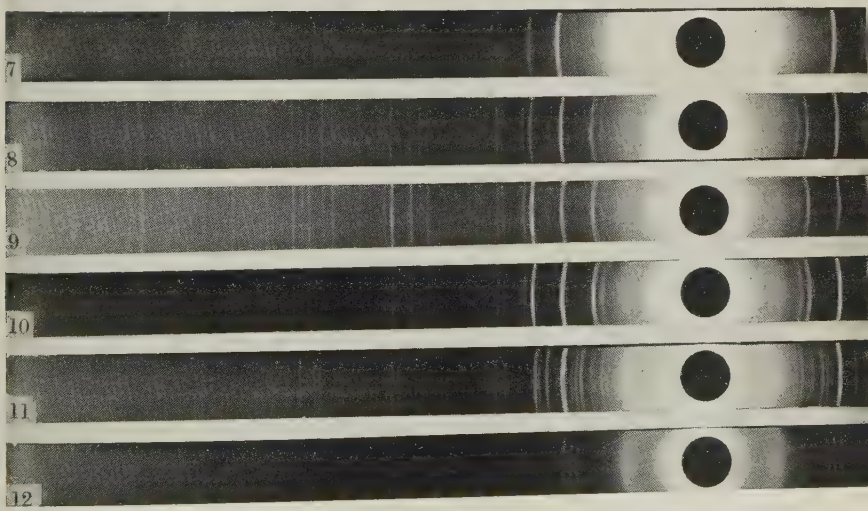
Our first experience of this mineral and the other potassium aluminium silicates, kaliophilite, and leucite was during an examination of samples taken from a scaffold which was removed from no. 1 blast furnace at Appleby-Frodingham in August 1945. The minerals were identified by

[1] Alfred Hartley Jay (1906–47) had been working on this same problem and this appendix contains his notes dated February 19, 1947. He died on February 26, 1947, after a motor-car accident on February 22. Two papers by him in this Magazine (1944, vol. 27, pp. 54 and 56) gave much promise of further useful work.






G. R. Rigby and H. M. Richardson: Artificial Kalsilite, &c.

means of X-ray data given in the X-ray card index (data by Bannister). In this scaffold the minerals kalsilite and kaliophilite were present in zones, but the reason for their localized appearance was not apparent. Thin layers of almost pure kalsilite were found in samples of slagged fireclay bricks which had been removed from the stacks of other blast furnaces at Appleby-Frodingham and at the Kettering Iron and Coal Co., Ltd. This note records accurate line spacings and chemical analysis of a well-crystalline and reasonably pure sample, and provides confirmation of Bannister's data, minor changes being due to the effects of different chemical composition. Chemical analysis of the kalsilite gave:

| $SiO_2$. | $Al_2O_3$. | FeO. | MgO. | $Na_2O$. | $K_2O$. | $H_2O$(<300° C.) | C. | traces. |
|---|---|---|---|---|---|---|---|---|
| 36·0 | 29·8 | 0·35 | 0·2 | [n.d.] | 27·0 | 0·5 | 4·0 | <0·1% |
| 0·599 | 0·292 | 0·005 | 0·005 | — | 0·287 | molecular ratios. | | |

X-ray powder data for kalsilite calculated from $a$ $5{\cdot}150_5$, $c$ $8{\cdot}684_5$kX ($c/a$ 1·686), with observed intensities. Bravais indices omitting the third index.

| *hkl*. | Intensity. | *d* (kX). | *hkl*. | Intensity. | *d* (kX). |
|---|---|---|---|---|---|
| 002 | wm | 4·342 | 215 | m | 1·2097 |
| 101 | m | 3·968 | 312 | m | 1·1898 |
| 102 | s | 3·112 | 313 | wm | 1·1376 |
| 110 | ms | 2·575 | 224 | w | 1·1075 |
| 111 | wm | 2·469 | 401 | vw | 1·1061 |
| 103 | w | 2·428 | 402 | wm | 1·0800 |
| 200 | vw | 2·230 | 108 | wm | 1·0548 |
| 112 | w | 2·215 | 403 | vw | 1·0406 |
| 004 | m | 2·171 | 306 | w | 1·0371 |
| 201 | w | 2·160 | 321 | vvw | 1·0163 |
| 202 | w | 1·984 | 315 | m | 1·0077 |
| 104 | vw | 1·952 | 217 | vw | 0·9992 |
| 113 | w | 1·924 | 322 | vw | 0·9961 |
| 203 | w | 1·767 | 208 | wm | 0·9761 |
| 114 | wm | 1·660 | 410 | wm | 0·9733 |
| 211 | | 1·655 | 009 | w | 0·9650 |
| 105 | m | $1{\cdot}618_5$ | 323 | | 0·9648 |
| 212 | m | $1{\cdot}571_5$ | 226 | m | 0·9621 |
| 204 | w | $1{\cdot}555_5$ | 316 | vw | 0·9404 |
| 300 | m | 1·487 | 405 | wm | 0·9384 |
| 213 | w | 1·457 | 324 | m | 0·9256 |
| 205 | wm | $1{\cdot}370_5$ | 218 | ms | 0·9127 |
| 214 | w | $1{\cdot}331_5$ | | | |
| 220 | wm | $1{\cdot}287_5$ | | | |
| 116 | ms | 1·2618 | | | |
| 304 | wm | 1·2267 | | | |
| 311 | | 1·2247 | | | |

s = strong; ms = moderately strong; m = moderate; wm = weak moderate; w = weak; vw = very weak; vvw = just visible.

The authors thank Mr. F. H. Saniter, Director of Research, for permission to publish this information, and Prof. C. E. Tilley for assistance in the identification of the kaliophilite.

# *Cuspidine from dolomite contact skarns, Broadford, Skye.*

By C. E. Tilley, F.R.S.

With chemical analyses by H. C. G. Vincent.

Department of Mineralogy and Petrology, University of Cambridge.

[Read January 23, 1947.]

CUSPIDINE was first described by Scacchi (1876) in the ejected blocks of metamorphosed limestone at Vesuvius, but a detailed and systematic morphological description of well-terminated crystals was given first by vom Rath (1883) from material at Cozzolino in Resina, Vesuvius. The monoclinic character of the spear-shaped crystals was then established with $a:b:c = 0{\cdot}7243:1:1{\cdot}9342$, $\beta = 89° 22'$, and twins on (100) giving $c:\underline{c} = 1° 16'$. Scacchi (in Arzruni, 1877) had earlier indicated the possibility that cuspidine he had described as orthorhombic was monoclinic and twinned when he recognized a re-entrant angle of 178° 42′ on the cleavage truncating the acute ends of the crystals.

Groth's optical data (in vom Rath, 1883) supported the monoclinic character with the optic axial plane (010) and $\gamma:c = 5° 30'$ in the acute angle $\beta$. Inclined dispersion.

Both Scacchi and vom Rath had recognized the essential composition of cuspidine as a calcium fluosilicate, but a more complete analysis was given much later by Zambonini (1910). Meantime C. H. Warren had analysed in 1899 a mineral from Franklin Furnace, New Jersey, the analysis of which was discussed by Palache (1910, 1935). He recognized it as that of a cuspidine to which he assigned in the first place a formula $Ca_2Si(O,F_2)_4$ already suggested by Dana (1892). Zambonini's analysis yielded him the formula $Ca_4Si_2O_7F_2$ which was later accepted by Palache (1935) for the Franklin Furnace mineral. This formula is that at present recognized in the literature. In none of the existing analyses to date is there any record of a determination of water. Warren's material was associated with nasonite; the mineral had a density between 2·965 and 2·989, but no material was left after analysis for the determination of other physical or optical properties. It is clear, however, that there is room for little water in either Warren's or Zambonini's analyses.

Larsen (1921) first reported on the refractive indices of the Vesuvian material with the data $\alpha$ 1·590, $\beta$ 1·595, $\gamma$ 1·602, $2V_\gamma$ 62°, $r > v$.

The mineral custerite was first described by Umpleby, Schaller, and Larsen (1913) from a limestone contact (inclusion in granite-porphyry) in Custer Co., Idaho. Their analysis gave the results $Ca_4Si_2O_7(F,OH)_2.H_2O$ thus identical with that of cuspidine except for the additional $H_2O$. These authors recognized a repeated twinning on (001) and a comparison of the optical properties of custerite and cuspidine was given as follows:

| | $\alpha$. | $\beta$. | $\gamma$. | $\gamma-\alpha$. | 2E. | Sign. | Extinction. | Twinning. |
|---|---|---|---|---|---|---|---|---|
| Cuspidine ... | 1·590 | 1·595 | 1·602 | 0·012 | 110° | + | 5° | (100) |
| Custerite ... | 1·586 | 1·589 | 1·598 | 0·011 | 105° | + | $6\frac{1}{2}$° | (001) (polysynthetic) |

with the optic axial plane in cuspidine (010), $\beta = b$, $\gamma : c = 5°$, cleavage (001); and for custerite $\alpha = b$, $\beta : a = 6\frac{1}{2}°$, cleavage (001) and prismatic.

Since this time custerite has been described from a number of limestone contact-zones including Crestmore, California (Tilley, 1928), and Carlingford, Ireland (Osborne, 1932), while cuspidine has been reported from the Alban Hills, Rome (Stella Starrabba, 1913), and much more recently from the Lower Tunguska river in Siberia associated with spurrite and merwinite (Sobolev, 1935). The striking resemblance in the optical properties of cuspidine and custerite has been commented on by more than one writer and has led to the suspicion that the two minerals might indeed be identical.

In a recent investigation of the skarn zones in the Durness limestone at its contact with the Beinn an Dubhaich granite near Broadford, Skye, Professor W. Q. Kennedy and the writer have recognized a custerite-like mineral forming an important constituent in a large number of the skarn zones. The description of the metasomatic phenomena associated with the dolomite contact-zones of the Broadford area will be given later by Kennedy and myself: here I shall present data identifying the mineral, leaving the details of its paragenesis to the forthcoming contribution.

Examination of the properties of the mineral shows that it must be designated as cuspidine. It occurs associated in the skarns with magnetite, diopside, wollastonite, calcite, and other minerals, and is developed as lanceolate crystals like the Vesuvian mineral (fig. 1). On the other hand, polysynthetic twinning, as seen between crossed nicols, is its most striking character, in that resembling the descriptions of custerite. The mineral behaves as a monoclinic crystal, cross-sections of the spears

showing the emergence of the acute bisectrix $\gamma$. In sections parallel to the optic axial plane the polysynthetic lamellae (taken as parallel to (001)) give symmetrical extinction $\alpha$:(001) = 6°. Twinning on (100) is also present in some sections. These data are summarized with other optical determinations as follows: $\alpha$ 1·591, $\beta$ 1·595, $\gamma$ 1·603, $2V_\gamma$ 60°, $\alpha$:(001) = 6°, $\beta = b$, dispersion $r > v$. These properties are clearly those of the Vesuvian cuspidine.

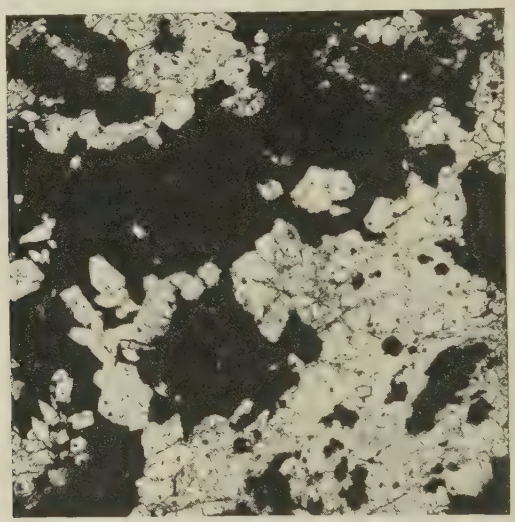


Fig. 1. Cuspidine in magnetite skarn, Kilchrist, Skye (×27 diams.). Typical lanceolate crystals of cuspidine set in magnetite which has intergrown bornite.

Examination of cuspidine from Vesuvian specimens has shown that, while simple twinning on (100) is dominant, a polysynthetic twinning is also present. This feature has previously been recognized by Cesàro (1928). Cuspidine with the optical characters given above has been isolated from a cuspidine-diopside skarn from Camas Malag, Loch Slapin, Skye, and analysed. At the same time cuspidine from an ejected block of skarn from Monte Somma, Vesuvius, has also been isolated and analysed, in order to be clear as to its water content. Both analyses have been carried out by Mr. H. C. G. Vincent and are set out in the following table, p. 93.

Examination of these results reveals the chemical identity of the two minerals and that the analyses conform to the formula $Ca_3Si_2O_7F_2$ in which there is little replacement of F by OH. If the small amount of

$H_2O+$ is taken into account in these two analyses the ratios become 1·99:3·95:2·14 and 2·00:3·94:2·12 respectively.

| | I. | Mol. ratios. | Less $CaCO_3$. | Metals to 9(O,F,Cl). | II. | Mol. ratios. | Less $CaCO_3$. | Metals to 9(O,F,Cl). |
|---|---|---|---|---|---|---|---|---|
| $SiO_2$ ... | 31·31 | 5218 | 5218 | 2·01 | 31·79 | 5298 | 5298 | 2·01 |
| $R_2O_3$ ... | 1·64 | — | — | — | 1·53 | — | — | — |
| CaO ... | 59·05 | 10544 | 10371 | 3·99 | 59·16 | 10564 | 10424 | 3·96 |
| MgO ... | 0·11 | — | — | — | nil | — | — | — |
| Alkalis ... | 0·15 | — | — | — | trace | — | — | — |
| F .. ... | 9·80 | 5158 | 5186 | 1·99 | 10·05 | 5289 | 5289 | 2·01 |
| Cl ... | 0·10 | 28 | | | trace | — | — | — |
| $CO_2$ ... | 0·75 | 173 | — | — | 0·62 | 140 | — | — |
| $H_2O+$ ... | 0·41 | — | — | — | 0·28 | — | — | — |
| $H_2O-$ ... | 0·33 | — | — | — | 0·16 | — | — | — |
| | 103·65 | | | | 103·59 | | | |
| Less O = F(Cl) | 4·13 | | | | 4·23 | | | |
| | 99·52 | | | | 99·36 | | | |
| Sp. gr. ... | 2·95 | | | | 2·97. | | | |

I. Cuspidine in cuspidine-diopside skarn, Camas Malag, Skye.
II. Cuspidine in skarn, ejected block, Monte Somma, Vesuvius.

*Synthesis of cuspidine.*—The accidental synthesis of cuspidine has been reported in an electric welding slag by Lapin (1941) who has detailed its properties. The slag consisted of cuspidine, fluorite, villiaumite, with perovskite and chrome-spinel and was formed as a thin crust on a welding seam at the expense of a fusion of the charge (42 % $CaF_2$, 36 % chalk, 4 % ferromanganese, and 18 % soluble glass) placed on the metallic electrode. Cuspidine, the chief component, crystallized as elongated crystals or characteristic lanceolate (simple) twins (100), and polysynthetic on the third pinakoid. The mineral may indeed be readily synthesized by sintering together $CaCO_3$ and $SiO_2$ in the proportion 3:2 with excess $CaF_2$ at 1140° C. when a product is obtained consisting of rounded grains of fluorite with interstitial cuspidine (0·1 mm. diam.) appearing as irregular crystals flattened parallel to (001) or spear-shaped and showing simple and repeated twinning parallel (001). These synthetic cuspidine crystals enclose minute drop-like grains with optical properties that identify them as larnite.

*Effect of heat on cuspidine.*—Cuspidine heated to 1200° C. overnight is converted into fine polycrystalline aggregates of larnite showing the characteristic fine repeated twinning of that mineral. The same effect can be seen in rock sections carrying cuspidine similarly heated. Here the development of larnite begins on the edges of the larger grains and along fractures within the crystals. The identity of the product of

heating has been confirmed by comparison of X-ray powder photographs with those of larnite of Scawt Hill, Co. Antrim (fig. 2).

The foregoing data raise the question of the validity of custerite as a separate mineral. Through the kindness of Dr. F. A. Bannister of the Mineral Department of the Natural History Museum, South Kensington, I have been able to obtain a small fragment of the original custerite-bearing rock from Idaho. In slice the mineral is associated with magnetite, diopside, and a little yellow garnet: there are associated areas

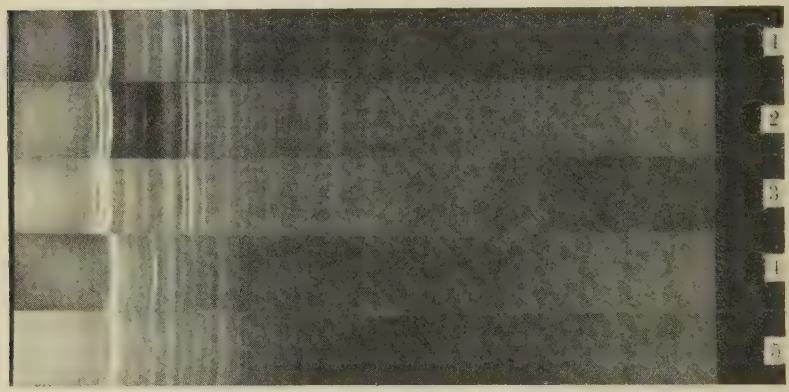



Fig. 2. X-ray powder photographs of: (1) Cuspidine (Skye), (2) Cuspidine (Vesuvius), (3) 'Custerite' = Cuspidine (Idaho), (4) Cuspidine (Skye), heated to 1200° C., (5) Larnite (Scawt Hill). Cu-$K\alpha$ filtered radiation; camera 9 cm. diameter ($\frac{5}{7}$ actual size).

rich in wollastonite which also occurs invested by the custerite. This custerite has beautifully developed polysynthetic twinning and shows in many of its sections the typical spear-shaped forms so characteristic of cuspidine. The mineral is, however, also developed flattened parallel to (001) and then shows negative elongation. A similar habit is found also in some of the Skye examples of cuspidine, and cuspidine occurs in that form in the synthetic product. The determination of the optical properties of the Idaho mineral shows that within the normal limits of error of the immersion method the refractive indices are identical with those of cuspidine, and further that the optic axial plane sections are those giving the symmetrical extinction $\alpha:(001) = 6°$. Obtuse bisectrix sections show parallel extinction. In its habit and paragenesis the Idaho mineral can be matched with the Skye examples of cuspidine. There can, I think, be little doubt that the Idaho 'custerite' is in fact cuspidine. This identity is further confirmed by X-ray photographs. Powder photo-

graphs of the analysed Vesuvian and Skye minerals, together with that of the Idaho 'custerite', are reproduced in fig. 2 for comparison.

The essential identity of the Idaho 'custerite' and a Vesuvian cuspidine on the basis of X-ray powder photographs had been indicated by Dr. F. A. Bannister to me when he had forwarded the specimen of the Idaho mineral now examined. In the same figure are also reproduced powder photographs of larnite obtained from heating the Skye cuspidine and the type larnite of Scawt Hill, Co. Antrim.

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# *An improved polarizing microscope. II. All-purposes model.*

By A. F. Hallimond, M.A., Sc.D., F.G.S.
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and E. Wilfred Taylor, C.B.E., F.R.M.S., F.Inst.P.
Messrs. Cooke, Troughton & Simms, Ltd., York.

[Read November 7, 1946.]

## I. *Introduction.*

In the description of an improved polarizing microscope, recently published by the present authors,[2] provision was made for the use of polarizing film in place of calcite prisms, and the consequent changes in the design of the substage and tube were discussed. The model then described was, however, of smaller size than is required for some patterns of Fedorov stage now in use, and a larger stand was under consideration. For technical reasons this could not be produced at the same time as the smaller instrument, and it was therefore necessary to postpone the description which forms the subject of the present supplementary paper. The changes involved are mainly dimensional, the optical and manipulative arrangements being in principle the same as in the smaller model, but the general standard of equipment in details such as stage racks, ball-bearing stage, and interchangeable bodies is on a scale corresponding with that in the largest existing types of stand. The general arrangement of the instrument will be readily understood by means of the photographs (figs. 1 and 2) and the sectional drawing (fig. 3). The following notes are therefore confined to a brief discussion of the special additional features.

## II. *The stand.*

The foot and limb are larger than in the previous model, and the hinge is provided with a lock. The focusing block carries a ball-bearing fine adjustment *A* (fig. 3) reading to 0·001 mm. and in front of this is a vertical slide with lock *B* which permits the interchange of monocular and binocular bodies, &c. A second slide has a rigid lock *C* by which the tube and focusing block can be fixed at a higher level, thus adding at

[1] Published by permission of the Director, Geological Survey and Museum.
[2] Min. Mag., 1946, vol. 27, pp. 175–185.

least 1½ inches to the working distance available for long-focus objectives or thick objects and for the universal stage. The various interchanges may entail a small displacement of the centre, but this should be corrected by means of the hand-centring screws at the bottom of the tube, while the common adjustment of the objectives in their centring holders is left undisturbed.

The fine adjustment operates only on the bracket *D* carrying the objective and analyser, while the replaceable part of the tube is attached by the slide *B* directly to the focusing-block. In this way the weight of the binocular body, &c., is borne only by the coarse focusing-rack, and the bodies can be interchanged without disturbing the adjustment of a high-power objective.

### III. *The substage.*

Rack-focusing is provided, but otherwise the equipment conforms to that already described in the smaller model. In the latter the condenser is focused by movement in a sleeve having a firm locking-screw. This is fairly rapid and effective for occasional use, but for some purposes, especially in connexion with phase-contrast methods, it is useful to have the condenser and swing-out fittings on a rack of usual type. An additional slide *E* permits the interchange of the complete substage and stage, and is provided with locks of a specially rigid type. On both models the mirror has locking-heads which prevent it from being accidentally disturbed during the manipulation of the substage.

### IV. *The stage.*

An accurate ball-bearing stage is provided, with a lock and adjustable resistance to rotation, tappings to receive screws for attaching the universal stage, &c. The outside diameter is 120 mm., with two verniers. This relatively small diameter has been adopted since a stage wide enough to extend beyond the base of the largest Fedorov stage becomes inconveniently large for routine use. A rack *F* with lock allows the usual adjustments for ore-microscopy and for the universal stage, while the special slide *E* already mentioned permits the interchange of the complete stage.

### V. *The tube.*

Two interchangeable bodies are available, the monocular body being most suitable for determinative measurements, while the binocular gives greatly improved comfort for prolonged use.

*Monocular body.*—This substantially follows the design of the smaller

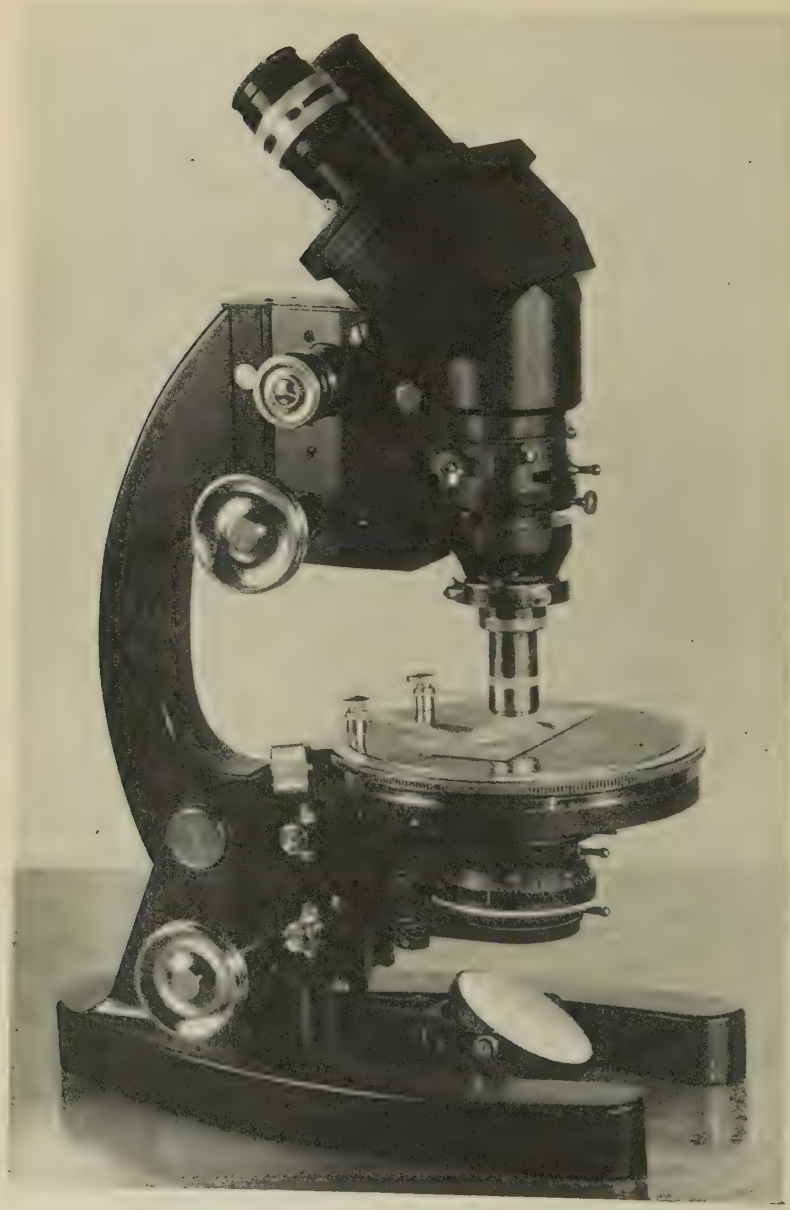

FIG. 1. Large polarizing microscope with binocular body.

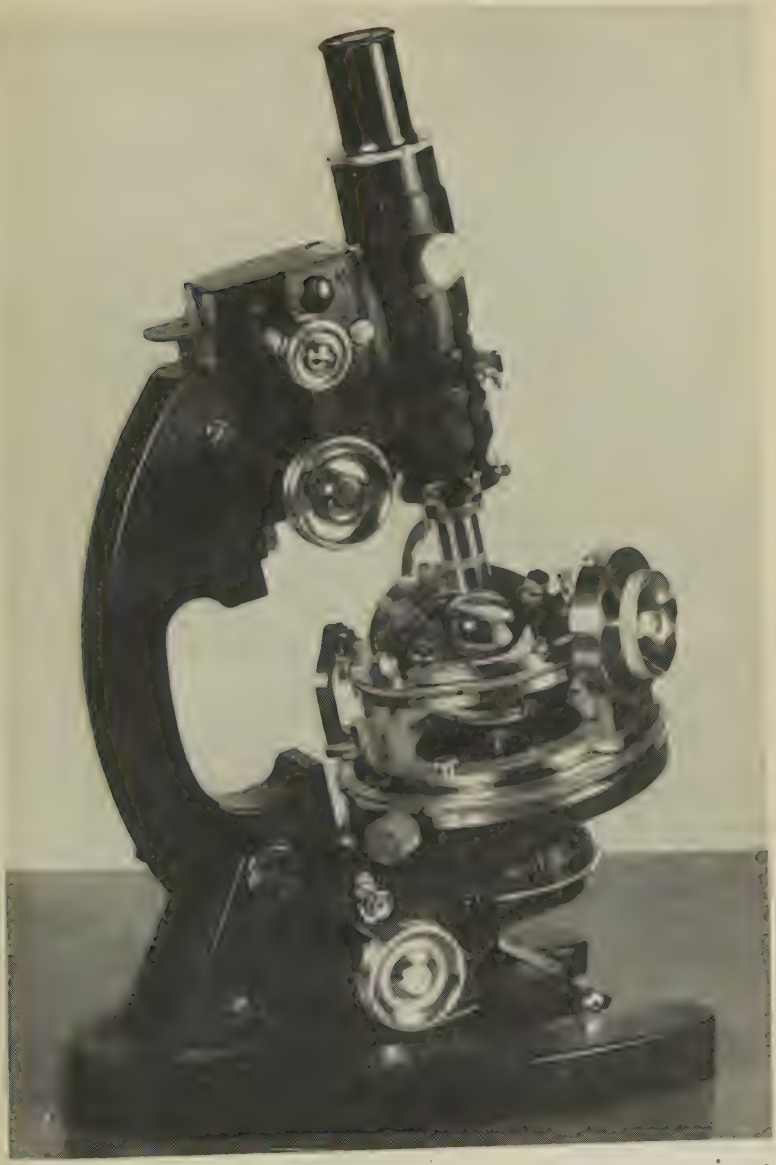

Fig. 2. Large polarizing microscope with monocular body. Stage rack lowered. Focusing-block partly raised, to accommodate a four-circle universal stage.

model, with the new type of Bertrand lens fitting, and with provision for inserting the vertical illuminator without increasing the tube length. The special determinative methods available have already been indicated in the first part of this paper. The analyser is rotatable. For most mineralogical work, even in ore-microscopy, the desired result can be obtained by rotating the polarizer through a small angle, and there are certain advantages in having a fixed analyser as a datum for the adjustment of the rest of the reflecting and polarizing system. Nevertheless, there is some increased facility in the rotating analyser and this has accordingly been fitted. An important consideration, affecting more particularly the biological side, is the possible use of the rotation in conjunction with phase-contrast equipment. For ore-microscopy, however, care must be taken to see that the analyser has been turned to the orientation which is most efficient for use with the reflector unit. This is specially important in using the new coated cover-glass, which is preferable to the prism on account of its better aperture relations, but has a rather marked polarizing action.

*Binocular body.*—Apart from giving increased personal comfort for the observer, the binocular eyepiece affords improved contrast in the image. This probably results from the elimination of the grey background which is contributed by the unused eye, and which obscures the darkest parts of the image seen by the other eye.

In prismatic binocular eyepieces the beam is divided by an inclined half-reflecting surface, usually coated with rhodium. Approximately half the light is thus sent to each eyepiece, but the surface has an appreciable polarizing action, the light in one eyepiece being enriched in one component while that in the other eyepiece has a corresponding deficiency. This polarization is parallel to the principal planes of the prism and therefore of the microscope, so that the only effect produced by it when the analyser is in position in crossed or parallel orientation is a small difference in illumination. If, however, the analyser is 'out' there remains a weak analysing action due to the prism, and this gives rise to weak interference colours which are superimposed on the image as usually seen with the polarizer alone. In one eyepiece the colours are those for the crossed position, in the other they are complementary as for the parallel position. When the two images are combined in binocular vision these colours compensate one another, but incomplete combination is very common and the faint tints which are then visible may be a source of annoyance. The effect can be eliminated by inserting weakly polarizing plates, if desired.

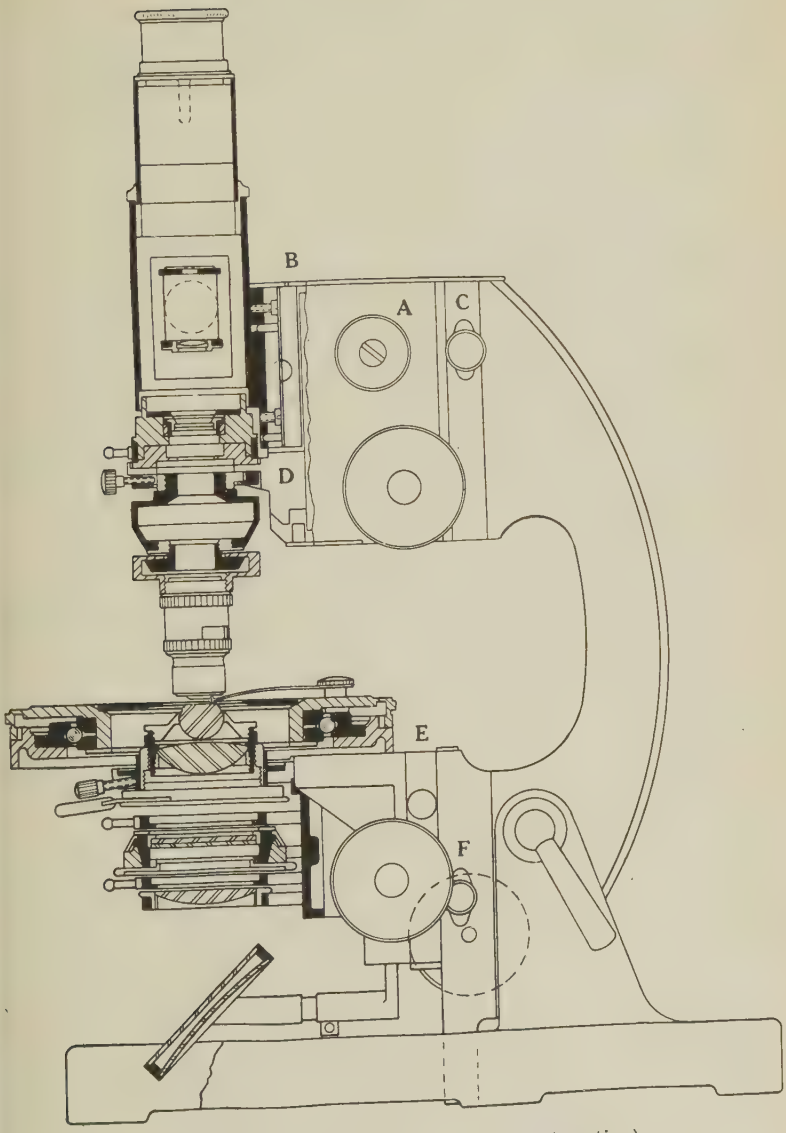


FIG. 3. Large polarizing microscope (part section).

It is not easy to fit a Bertrand lens of sufficiently low magnification, but the interference figure can be examined by removing one of the eyepieces, or by means of a Becke lens in the usual way.

The prisms entail an increase of tube length, to an extent depending on the height and construction of the optical system. So far as the objective corrections are involved, the increased length is compensated by an additional lens placed between the objective and the prisms, so that in this respect there is no adverse effect. There remains, however, an increase in the magnification which in practice cannot be reduced below about $1\frac{1}{2}$ times that obtained from the same objective and eyepiece in a standard monocular tube. This is usually neutralized by the employment of low-power eyepieces (say, $\times 4$) or, if more powerful eyepieces are preferred because of their wider field, the objectives chosen may be of somewhat lower power than usual. With the highest powers the gain in magnification is helpful, the tendency in routine work being to retain the $\times 5$ or $\times 7$ eyepiece although the objective will allow the use of $\times 10$ or $\times 15$ with consequent improvement in the visibility of the smaller structures.

## VI. *Use of the universal stage.*

Fedorov stages of the largest type can be used. Standard tappings are provided; it may be necessary, however, to employ special fixing screws on account of the difference in thread. If the universal stage fails to clear the frame of the microscope when the slide at *C* has been raised (fig. 2) the clearance can be increased by lowering the stage rack.

To adjust the illumination the condenser may be removed; the desired aperture, usually about 0·2 N.A., is then supplied by the weak collective lens aided by the diffuser. R. C. Emmons[1] recommends the insertion of a ground glass, but no special accessory is here required, the diffuser in its swing-out fitting being already provided. Special objectives designed for the existing stages can be used since they are not sensitive to small changes of tube length. The iris diaphragm is removable with the condenser, but if a diaphragm is required in this position a disk with the required opening can be inserted in one of the swing-out fittings.

For refractive index determinations of the very highest accuracy, direct illumination is best obtained from a distant source or from the monochromator. For ordinary determinative work, when the condenser is in use, a satisfactory Becke line can be obtained by closing the iris

[1] R. C. Emmons, The universal stage. Mem. Geol. Soc. Amer., 1943, no. 8, pp. 39 and 98. [M.A. 9–18.]

diaphragm. By means of the universal stage the available methods, especially for refractive-index measurement, have been considerably extended; they do not, however, entail any change in the construction of the microscope, and reference should be made to text-books such as that of Emmons (loc. cit.).

### VII. *Phase-contrast microscopy.*

During the past ten years a substantial improvement of the image has been obtained for small transparent objects which differ to a moderate degree in refractive index from the surrounding medium. 'Relief', as usually recognized in mineral preparations, can be diminished, and part or all of the object stands in marked contrast with the background, being usually darker. The apparatus used consists of an annular diaphragm placed under the condenser and a special annular 'phase-plate' which is placed at the upper principal focus of the objective. For regular use the phase-plate is built into the objective and a special condenser includes the required range of annular diaphragms. The method, which is still undergoing development, has already achieved outstanding success in biological research and may well become of interest for mineral problems, though cases depending on the form of minute structures are of less common occurrence: a possible example is the study of dust particles.

# *Flavus or blavus: a difficulty in understanding early descriptions of minerals.*

By C. E. N. Bromehead, B.A., F.G.S.
Geological Survey of Great Britain.

[Read November 7, 1946.]

WHILE studying some of the early works on minerals I came across an obvious difficulty: several minerals, amongst which lapis-lazuli is the most startling, are described in Latin as *flavus*, yellow or flaxen-coloured, not blue. This error has been copied into a book in English. The solution is less obvious than the difficulty, and it may therefore be worth while to put it on record for other workers on similar lines.

The 'Liber mineralium' of Albertus Magnus (or St. Albert) (3),[1] written about A.D. 1250, is one of the most important of the post-classical works, in that, besides repeating the descriptions and some of the supposed medical and magical properties of minerals, it includes a number of personal observations on localities, modes of occurrence, &c. Book II, tract II, is a description of precious stones and their virtues, the stones being given in alphabetical order of their names. This arrangement was followed by most authors, including Leonardus (8; see below), until Conrad Gesner (5), who in 1565 published the first work on minerals and fossils to be illustrated with figures. He attempted a scientific arrangement and described the alphabetical as 'nimis vulgatum & trivialem', the last word in approximately its original sense.

In Cap. XVII (letter S) Albertus describes Saphirus [*sic*]. It is clear that he is dealing with our sapphire, not with that of Pliny which is lapis-lazuli; he says that in colour it is a clear yellow (perspicuus flavus), like the sky on a fine day. From the comparison with the sky it is certain that the word printed as *flavus* must mean blue. Equally certain is the description in Cap. XX of the mineral Zemech, also known as Lapis laxuli [*sic*], from which azure is made: it is a fine *flavus* colour with little golden specks (pyrite). Under Hyacinthus (Cap. VIII) we learn that there are two chief kinds, the watery (aquaticus) and the sapphirine, the colours of which are respectively whitish and very bright *flavus*. Whether Hyacinthus is corundum, or zircon, or both, or neither, is one of the more difficult questions in early mineralogy: it is

[1] Numbers refer to list of works at the end of this paper.

fully discussed by C. W. King (7*a*, pp. 160–168; *b*, pp. 242–257), but the colour should be blue, not yellow. The same adjective is applied (Cap. XIX) to turquoise.

These quotations are taken from the latest text of Albertus (3*a*), but I have confirmed that the important word is the same in editions printed in 1518 and 1541. It may be advisable to state that the 'Liber mineralium' is a genuine work of Albertus and is not to be confused with a spurious and ridiculous treatise, 'De secretis mulierum . . . lapidum . . .', which was constantly reprinted and translated and became known in France as the 'Grand' or 'Petit Albert', beloved of fortune-tellers and interpreters of dreams. I have not examined texts of the genuine work earlier than 1518, but the word *flavus* must be printed in some, if not all, of these.

In 1502 Camillus Leonardus (8) of Pisa published at Venice the first edition of his 'Speculum lapidum'. Other editions in 1516, 1533, 1610, and 1717 are listed by Adams (1), who reproduces the title-page of the first of these. This evidently popular handbook is stated by the author to be compiled from the works of Aristotle,[1] Pliny, Albertus Magnus, and others: *flavus* is used in the first edition of lapis-lazuli, and the whole description is taken from Albertus. In 1750 Leonardus's book was translated into English with the title 'The Mirror of Stones'. Copies are not uncommon: the libraries of the Natural History Museum, the Geological Survey and Museum, and the Geological Society all have one; probably many members of the Mineralogical Society possess this book or have consulted it. It contains (p. 239) the following description:

'*Zumemellazuli*, or *Zemech*, but in *Latin* is the Stone *Lazuli*. This Stone is yellow, of the Colour of the Sky when it is in its greatest Serenity, not transparent, and shines with golden Streaks; it sustains the Fire, and from its Beauty is called the celestial or starry Stone. Being prepared by Physicians, it cures melancholy Disorders. There is also made of it a Colour call'd the Ultramarine Azure.'

There can be no doubt but that the description is of lapis-lazuli, but neither that mineral nor the sky on a fine day can be called 'yellow'.

*The solution of the difficulty.*—When I first came across this difficulty in understanding Albertus I wondered whether the word *flavus* had in medieval times changed its meaning; but this guess was wrong. Another possibility was a printer's error. I consulted several scholars, one of whom suggested that I should search the appendix to a recent

[1] i.e. the Pseudo-Aristotelian work in Latin translated from the Arabic of Avicenna: see E. J. Holmyard and D. C. Mandeville, Avicennae de congelatione et conglutinatione lapidum. Paris, 1927. [M.A. 3–466.]

edition of Du Cange's (4) glossary of medieval Latin, which includes a list of all words for colours. This gave the answer at once. Classical words for colours are notoriously few and often indefinite. Albertus was essentially German and used a latinized word Blavus, formed from the German blau or blaw. Whether he coined it himself or found it in use is uncertain and immaterial; both Du Cange and Hofmann (6) give, as a first reference for 'Blavus', Johannes Monachus, who died at Avignon in A.D. 1313 and was thus practically contemporary with Albertus: he used it in his life of St. Odo to describe certain vestments—'of the colour which we, in the vulgar tongue (vulgo) call blavus'. But despite this comment the word does not appear to have been common, except (with derivatives) in botanical works. In 1297 Matthaeus Silvaticus used Blavus in describing two plants, one of which is woad; Ruellius several times in a Latin version of the Greek Herbal of Dioscorides (Basle, 1537) to translate *κύανος*. Littleton's 'Latine dictionary' (9) gives Blaveolus as the 'the blew bottle, a flower', i.e. the cornflower. It is curious how the pursuit of one error leads to the detection of another: he puts this word in his Part II—Latine Classical, not in Part IV—Latine Barbarous; but his authority for the word is Hadrianus Junius, a Dutch medical man who died in 1575. I am indebted to Dr. L. J. Spencer for finding it thus misplaced, when I had concluded that Littleton did not give it. Salmasius (1588–1653), the commentator on many classical authors, places Blavus, as an adjective of colour, between Caeruleus and Purpureus.

It is strange that the early German mineralogists did not use the word. Agricola (2) uses 'Caeruleus' for the colour of Cyanus, Sapphirus, &c. Gesner (5) and his friends, whose books he printed with his own, used neither 'blavus' nor 'flavus' for blue, although one of them, Rueus, Doctor Medicus Insulanus (i.e. François de la Rue, a doctor of medicine of Lille), uses (p. 33) the exact words of Albertus for Sapphirus—the colour of the sky on a most serene day. Presumably he used a printed edition of the 'Liber mineralium' and omitted *flavus* because it made nonsense of the passage. Perhaps this note may safeguard future students of the history of mineralogy from the same misfortune.

In justice to the printer whose error has persisted for four centuries (so far!), it may be pointed out that in early type the character for F–l with ligature and serifs looks not unlike a B. What he printed had considerable resemblance to the manuscript he used.

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*Note.*—Since this paper was written I find that C. W. King was aware of the difficulty, but not of the solution. In 'Antique gems', 1860, p. 422, he writes: 'It is curious that Camillo [Leonardus], both in this place and in speaking of the Sapphire and Turquois, uses *flavus* as synonymous with *coelestis*, azure.'

# *Pyrophanite from the Benallt mine, Rhiw, Carnarvonshire.*

By W. Campbell Smith, M.C., T.D., M.A., Sc.D.
and G. F. Claringbull, B.Sc., Ph.D.
Department of Mineralogy, British Museum.

[Read November 7, 1946.]

PYROPHANITE was recorded by one of us in a recent paper[1] as one of the minerals occurring at the Benallt manganese mine in the vein from which material for the chemical analyses of the new manganese-rich chlorite, pennantite, was separated. As this was only the third record of pyrophanite in the world it seems necessary to give, very briefly, the evidence for its identification.

The original description of pyrophanite is that by A. Hamberg[2] (1890), who described the mineral, discovered by himself and G. Flink, as forming thin, deep-red plates, only about 0·15 mm. thick in drusy cavities in manganese ore at the Harstig mine, Pajsberg, near Persberg, Wermland, Sweden. The mineral is there associated with ganophyllite, garnet, 'manganophyll', and later deposited calcite.

The only other record of the mineral is from the Piquery mine of the Queluz district, Minas Geraes, Brazil. Here O. A. Derby[3] found transparent red grains in carbonate-rich manganese ore 'composed of a carbonate (rhodocrosite?), an olivine-like silicate (tephroite) and spessartite'. They had the appearance of rutile, but gave strong characteristic reactions for both titanium and manganese.

During the examination of thin sections of the vein carrying pennantite, referred to above, a few small orange-yellow crystals were observed. They were remarkable for their very high birefringence and high refractive index. In the course of the separation of the pennantite for analysis a few of these crystals were found in the fraction of the powdered vein-material which sank in undiluted methylene iodide.

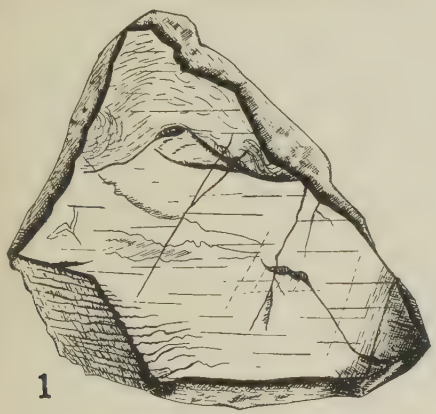
These crystals are very small, none exceeding 0·25 mm. in diameter, or 0·15 mm. in thickness. The habit is tabular with striations or traces

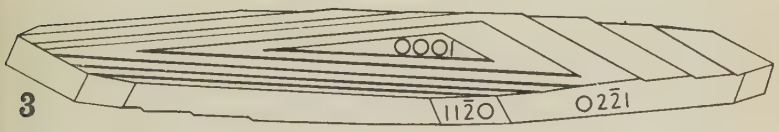
[1] W. Campbell Smith, Min. Mag., 1946, vol. 27, p. 218.

[2] A. Hamberg, Geol. För. Förh. Stockholm, 1890, vol. 12, p. 598.

[3] O. A. Derby, Amer. Journ. Sci., 1901, ser. 4, vol. 12, p. 21; 1908, ser. 4, vol. 25, p. 215.

of cleavage intersecting at 60° (figs. 1 and 2). Some show a trigonal outline. They are uniaxial, negative, with refractive index higher than 1·84 and very high birefringence. The optic axis is perpendicular to the crystal plates. No measurements could be obtained on two minute faces






Figs. 1 and 2. Pyrophanite from Benallt mine, Rhiw, Wales. Drawings of crystals showing indications of faces and, on the (0001) face, striations or traces of cleavage intersecting at 60°. Fig. 1. Camera lucida drawing, ×270. Fig. 2. Drawn over a photomicrograph, ×270.

Fig. 3. Enlarged reproduction of A. Hamberg's figure of pyrophanite from Harstig mine, Pajsberg, Sweden. (Geol. För. Förh. Stockholm, 1890, vol. 12, pl. 13, fig. 10.)

or cleavage surfaces on the edges of the plates, but the triangular striations and outlines suggested rhombohedral (or hexagonal) symmetry. No pleochroism was observed either in the isolated crystals or in the thin sections. The colour of a crystal 0·13 mm. thick is ochraceous-orange.

These characters suggested that the crystals might possibly be pyrophanite. Microchemical tests made by Dr. M. H. Hey on a single crystal, which was all that could be spared at that time, indicated the presence of manganese, but failed to give a definite reaction for titanium. A

later test, using several crystals of the mineral, gave distinct reactions for both manganese and titanium. The identification was definitely confirmed by X-ray photographs taken with unfiltered iron radiation; and, incidentally, additional confirmation of the presence of manganese was given by the absence of $\beta$-reflections on these photographs. The best photograph was obtained from six crystals (0·13–0·26 mm. in diameter) mounted in random orientation. A rotation photograph of these grains gave a powder diagram typical of an ilmenite-type structure. Direct comparison with an ilmenite photograph taken in the same camera showed that all the spacings for the mineral under examination were slightly larger. Measurements taken on the photograph of the Benallt mineral are in good agreement with the spacing and intensity data given by E. Posnjak and T. F. W. Barth[1] for artificial manganese titanate, $MnTiO_3$.

[1] Zeits. Krist., 1934, vol. 88, pp. 276–278. [M.A. **6**–45.]

# *Crystals of artificial cassiterite.*

(With Plate V.)

By J. J. Frankel, D.Sc., F.G.S.
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[Communicated by Dr. G. F. Claringbull; read January 23, 1947.]

THE crystals of artificial cassiterite, described below, were produced by volatilization of South African low-grade tin ores. In the sinter-pot method employed, air was blown through a charge of alternate layers of coke and of a 12 % metallic tin concentrate mixed with fine coke. This charge was placed above a basal layer of previously ignited coal. Occasionally sodium chloride was mixed with the concentrate to remove tin as chloride as well as oxide fume. The air-flow was carefully controlled to prevent slagging and was maintained until the evolution of copious fumes of tin oxide, and at times of chloride, ceased.

Optical pyrometer readings on the charges during the experiments gave temperatures of 1050° C. approximately, but it is certain that this value is a grave under-estimate of the actual temperatures in the interior of the sinter-pot. Petrov (1933), in his paper on artificial cassiterite, has given temperatures of 1300° to 1350° C., and it is possible that similar values may have been reached in the present case.

Voids in the loosely sintered residues contained nests of thin, colourless, transparent crystals (pl. V, fig. 1). Where incipient slagging of the charge had taken place the walls of the voids were coated with a dense white deposit of globules. Occasionally this deposit covered larger crystals (pl. V, fig. 2).

Goniometric measurements on the larger crystals were unsatisfactory because of surface imperfections on the faces, but they suggested the presence of the second-order bipyramid and prism faces. The data presented below were therefore obtained by microscopical study only.

The crystals may be divided into the following arbitrary morphological groups:

(*a*) Lath-shaped crystals either as individuals or in interlaced aggregates. These are 0·5–1·0 cm. long, 10–50 $\mu$ wide, and 4–15 $\mu$ thick.

(*b*) Hair-like crystals several cm. long but only 1–6 $\mu$ thick. The resolving power of the objective prevented the measurement of the lower limit of thickness.

(*c*) Elongated skeletal crystals either in rectangular growths or like geniculate twins. They may be up to 1 cm. long with a cross-section of 20–50 $\mu$ but are frequently only 4–8 $\mu$ thick.

(*d*) Pyramidal crystals 10–30 $\mu$ in width occurring on larger faces of lath crystals.

In addition there was the extremely fine-grained white 'powder'.

Most of the crystals of group (*a*) rest on one of a pair of well-developed parallel faces. They show straight extinction parallel to the length and give an eccentric uniaxial interference-figure, which suggest a pyramid face. A slice of quartz was cut at an angle of 34° to the plane of the horizontal axes to simulate the (101) face of cassiterite. The eccentricity of the optic picture in this orientated section was practically identical with that of the cassiterite crystals resting on a dominant face. Further, in cassiterite the plane angle formed on the face (101) by the faces (011) and ($0\bar{1}1$) is 79° 22′ (calculated). The average of 40 measurements of the corresponding angle on the dominant face of the crystals gave 78·7°. Measurements using a universal stage gave values of 33° to 36° for the inclination of this face to the horizontal axes. When the lath-like crystals were rotated about their length in a viscous medium (for example, Canada Balsam with 5 % xylene) the angle of extinction between the plane of the dominant face and that of the horizontal axes was determined as 34° to 36°.

The above methods of measurement have all established that the two dominant faces in the crystals of group (*a*) and in most of group (*b*) are of the second-order bipyramid *e* (101). The crystallography is simple; two well-developed elongated *e* faces with the other six faces of the same form as pyramidal terminations and two faces of the second-order prism *a* (100) are present. The idealized form is shown in text-fig. 1*a*, while text-fig. 1*b* is a camera lucida drawing which shows the appearance under the microscope. Most of the crystals are flared towards the terminations and where both ends are developed they have a 'dumb-bell' shape (text-fig. 2). Generally, however, only one extremity is present as the crystals have grown from a thicker individual.

Many of the group (*b*) crystals have the same habit, but the minute cross-sectional area of the majority makes a precise determination impossible. Their dominant form may be simply the second-order prism.

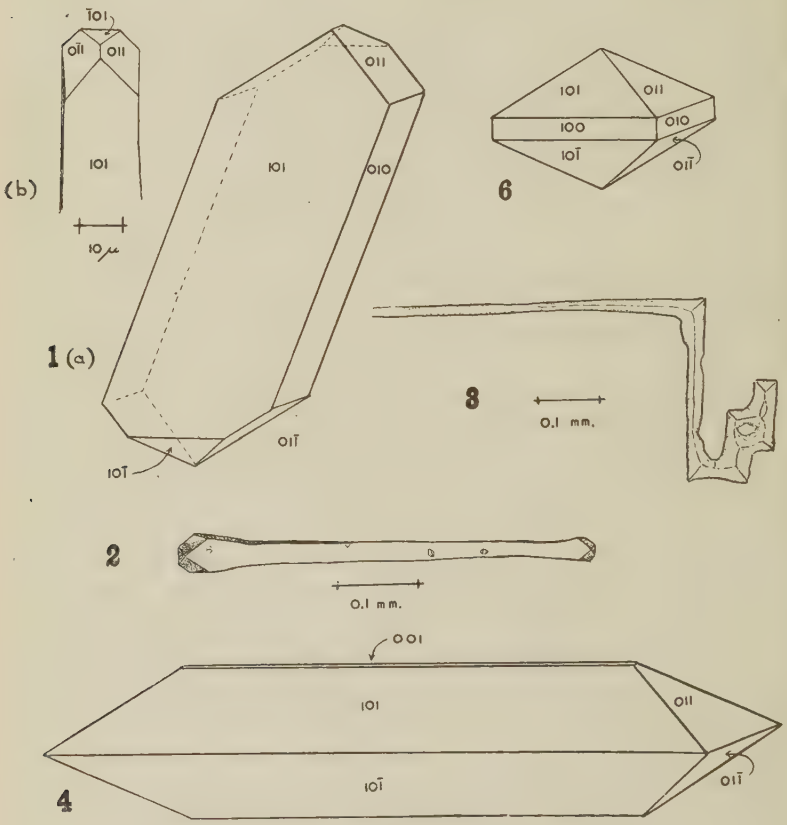
Crystals in group (*c*) exhibit two interesting habits. The first presents elongated prismatic crystals in rectangular or cruciform growths (text-fig. 3). The majority show isotropism or slight anisotropism when in the position they normally occupy on a slide. The almost perfectly centred interference-figure is generally anomalously biaxial, either showing a normal picture with a small optic angle or one centred straight brush in the 90° positions. Straight extinction is shown when the crystals are tilted slightly from the position of isotropism. The form in these crystals is also *e* (101) elongated parallel to one horizontal axis. A very narrow basal pinakoid bevels the crystals on rare occasions. The essentially skeletal nature of these crystals is evident from the holes present where the growth orientation changes through a right angle but remains in the plane of the horizontal axes. The first-order bipyramid, *s* (111) may be present as thin bevels to the *e* faces at these positions. The idealized form is shown in text-fig. 4.

Crystals of the second habit in group (*c*) are also skeletal. They are, in ordinary light, exactly like geniculate twins with two lath-like limbs meeting at 68°. This structure may be repeated several times (text-fig. 5*a*) or a limb may have off-shoots at 68° (text-fig. 5*b*). Text-figs. 5*c* and 5*d* are idealized forms. In polarized light the crystals show high-order colours, a flash interference-figure, and symmetrical extinction. The forms present are the second-order bipyramid and prism. The terminations of the limbs when present are composed of small *e* faces. On some of these crystals each of the *a* faces is replaced by two other pyramid faces, probably *s* faces (text-fig. 5*b*). Many of the crystals are broken and the fragments resting on the broad face show inclined extinction. Very small fragments may have given the erroneous impression of crystallization in systems other than tetragonal. (Hintze, 1904; Groth, 1906.)

The small perfectly formed pyramidal crystals of group (*d*), (text-fig. 6) a combination of the forms *e* and *a* are scattered without any definite orientation on the broad *e* faces of the larger flared crystals. They are sometimes elongated in the direction of a horizontal axis when they have a length of 50 $\mu$. This habit is identical with that of fig. 17 for cassiterite given by Goldschmidt (1923).

The white powder under moderate magnifications has an opaque appearance, which may obscure the transparent nature of crystals coated with it. Under highest powers it is seen to be composed of minute laths as well as crystals of the second habit of group (*c*), generally 2 $\mu$ and less in length. Interference colours are not always detectable. An X-ray

powder photograph revealed the structure of natural cassiterite, but the extremely small particle size was indicated by the broad lines of the X-ray pattern. This material may be regarded as tin oxide fume which



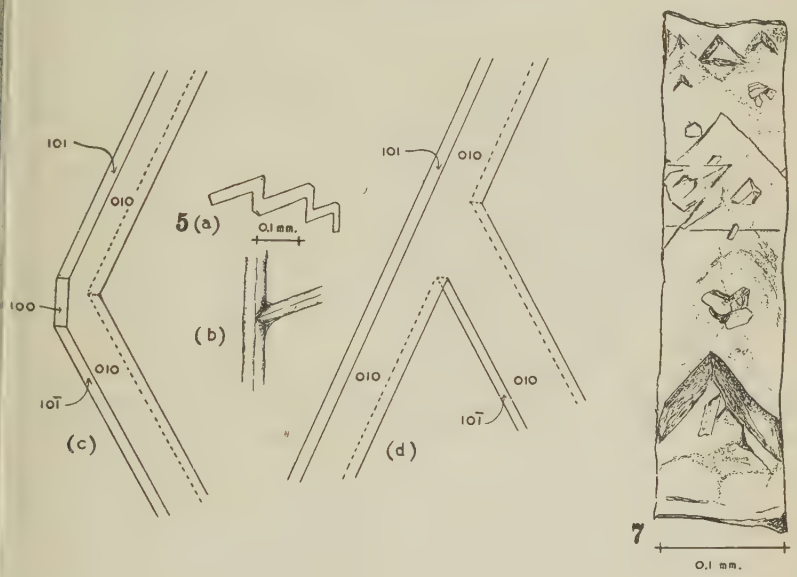

Figs. 1–4 and 6. Crystals of artificial cassiterite.

was retained in the charge; its appearance is similar to that of fume which was expelled from the sinter-pot and collected.

The combinations of the first-order bipyramid and prism, common to natural cassiterite do not occur on these crystals. The presence of elongated first-order prisms is doubtful, while the *s* face is absent except on some crystals of group (*c*). Although many crystals look like geniculate twins, they are actually simple single individuals; in fact no twin crystals were observed. These observations are similar to those made

by Himmel and Porter (1931). The artificial cassiterite crystals described by vom Rath (1867), which are simple forms of well-developed *e* faces, have some features in common with crystals in group (*a*).

X-ray patterns of aggregates of the present material showed no lines other than those of the natural tetragonal mineral.




FIGS. 5 and 7. Crystals of artificial cassiterite.

Growth accessories are common on the dominant *e* faces. They are generally elevated triangular areas on a stepped surface, with edges parallel to the *e* or *a* faces (pl. V, fig. 3 and text-fig. 7). Fine striations parallel to *e* faces are also present. The triangular depressions and hollow crystals found by Himmel and Porter (1931) were absent in these crystals, and no accessories were noted on faces of the other forms present.

A spectrographic analysis was kindly made by Mr. L. H. Ahrens who reported that a spectrographic trace of tungsten was the only significant impurity.

Uniaxial interference-figures are general except in those crystals of group (*c*) which are anomalously biaxial. In hand-specimen all the crystals appear to be colourless, but under the microscope thicker laths have a very pale purplish-brown colour. Dichroism is just visible in

these with $\epsilon$ pale purplish-brown and $\omega$ very pale purple. A West's high refractive index liquid of 2·06 showed that the indices were just above and somewhat below this value for Na light. Crystals which lie perfectly flat on a large *e* face show straight extinction and all have positive elongation. Small extinction-angles up to 6° were due to the imperfections on the *e* faces, which affected the normal resting position of such crystals on the slide. Strain may have contributed to this extinction-angle as well.

The morphological classification proposed by Shneider (1937) for the estimation of temperatures of formation could not be applied to the cassiterite in the present case, because of vast differences in the conditions and environment of the natural and artificial mineral. It is, however, likely that these artificial crystals were formed above 600° C., when the sintered mass cooled after the cessation of the air-flow. The description of crystal growth outlined by Davey (1934) applies very well in this case. Pl. V, fig. 4, shows the growth of secondary on larger primary crystals.

*Acknowledgements.*—I thank the Director of the Government Metallurgical Laboratory for permission to publish this paper. I am grateful to Mr. E. Mendelssohn and Dr. W. O. Williamson for suggestions on various occasions.

*Summary.*—Crystals of artificial cassiterite formed by volatilization from the natural mineral are described. Most of the crystals are simple combinations, of a second order bipyramid elongated along either horizontal axis or at right angles to this, with subordinate second order prism faces.

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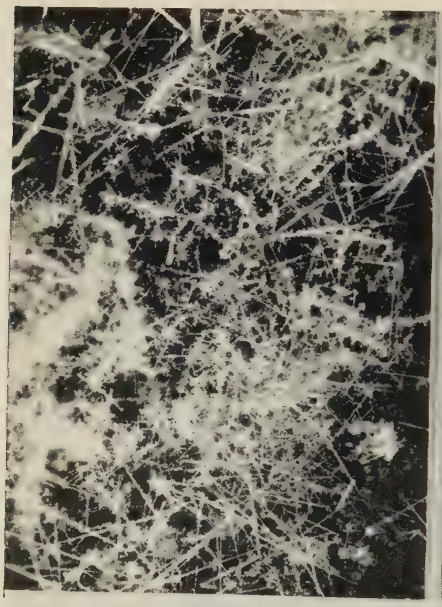

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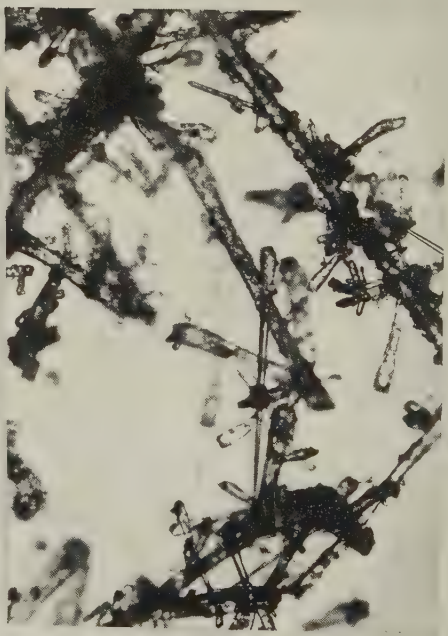

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Explanation of Plate V.

Fig. 1. Interlaced crystals of artificial cassiterite. ×5.

Fig. 2. Globules of fine white cassiterite 'powder' which also coats the crystals. ×5.

Fig. 3. Growth accessories on an *e* face.

Fig. 4. Association of primary and secondary artificial cassiterite crystals. ×110.

# *The occurrence of nigerite, a new tin mineral in quartz-sillimanite-rocks from Nigeria.*[1]

(With Plate VI.)

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Geological Survey of Nigeria.

[Read January 23, 1947.]

## I. Introduction.

A NEW tin mineral, which has been given the name 'nigerite', was discovered in June 1944 during an investigation of the tin-bearing pegmatites of Kabba Province, central Nigeria.[2] The chemical and physical properties of nigerite have been determined by F. A. Bannister, M. H. Hey, and H. P. Stadler, and their results will be published in the next number of this Magazine. Dr. Hey's analysis shows $SnO_2$ 25·33, $Al_2O_3$ 50·91, $Fe_2O_3$ 11·90, ZnO 4·51 %, &c., and the unit-cell contents are given by the formula $(Zn,Mg,Fe'')(Sn,Zn)_2(Al,Fe''')_{12}O_{22}(OH)_2$.

Nigerite is found as a common constituent in certain quartz-sillimanite-rocks associated with the tin-bearing pegmatites. Although locally abundant, nigerite is more likely to remain of scientific rather than economic interest. The principal occurrences are located in the uninhabited bush east of the Egbe–Lafia road, in the north-west corner of Kabba Province, central Nigeria (text-fig. 1).

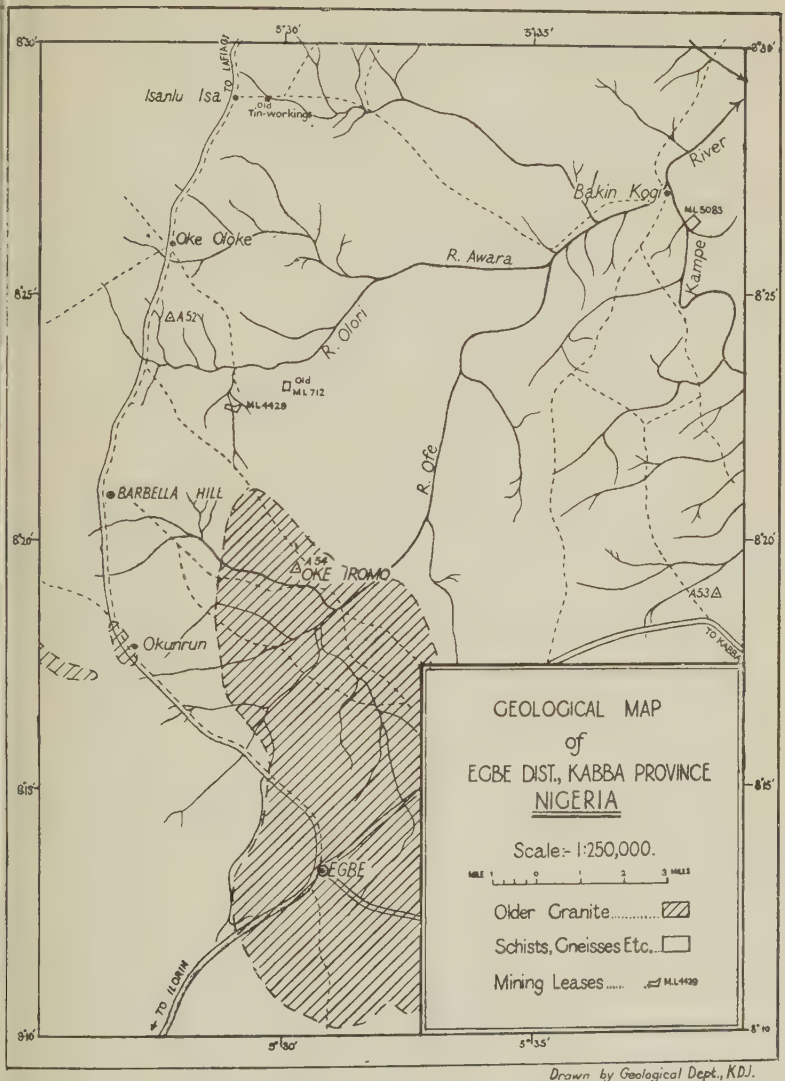
## II. General geology.

The area under consideration is composed of pre-Cambrian schists, gneisses, and granite. Tin-bearing pegmatites, genetically related to the granite, are well developed especially along the eastern marginal zone of the granite. The quartz-sillimanite-rocks, wherein nigerite was found, occur in close association with these pegmatites.

(i) *Schists.*—The schists represent a series of altered sediments. They include mica-, quartz-, and quartz-mica-schists, also quartzites and

[1] Published with the permission of the Director of the Geological Survey of Nigeria.

[2] This mineral was first mentioned in the Nigerian Geological Survey Annual Report, 1944.




TEXT-FIG. 1. Simplified geological and locality map of the area in which the nigerite-bearing rocks occur.

quartz-sillimanite-schists. Garnetiferous granulites and massive amphibolites are well developed locally. The regional trend of the foliation of these rocks is N.–S.

(ii) *Gneisses.*—The gneisses consist of banded granite-gneiss and soft felspathic gneiss, grading imperceptibly into schist.

(iii) *Granite.*—The Egbe Granite, which occupies the south-central part of this area, is a member of a suite of 'Older Granites', with which the tin-bearing pegmatites are genetically related.[1] The rock is a porphyritic biotite-hornblende-granite, which in places is distinctly gneissose. Pegmatites are particularly well developed around the eastern margin, and the granite itself is traversed by numerous small pegmatite dikes. It is interesting to note that the Older Granites, of which the Egbe outcrop is a member, are older than the Younger Granites of north-central Nigeria, with which the main period of tin mineralization is related.

## III. Pegmatites.

The detailed mineralogy and paragenesis of the pegmatites have recently been described by the authors.[1] The pegmatites may be divided into three groups, according to their mineralogical composition. They may be further subdivided into 'simple' and 'complex' varieties, depending upon the extent to which they had been affected by late-stage albitization. In addition to these three groups the pegmatite suite also includes quartz-tourmaline veins and quartz-sillimanite veins.

(*a*) *Microcline-quartz-pegmatites.*—The bulk of the pegmatites within the Older Granites are simple microcline-quartz types. They also occur in the schists and gneisses but they are not so numerous as the microcline-quartz-muscovite-pegmatites. The complex varieties sometimes contain cassiterite and columbite-tantalite.

(*b*) *Microcline-quartz-mica-pegmatites.*—The bulk of the economic deposits of cassiterite and columbite-tantalite occur in association with the albitized microcline-quartz-muscovite-pegmatites in the schists and gneisses. Microcline-quartz-*biotite*-pegmatites are well developed in the contact zone of the Egbe Granite. They are sometimes albitized to an appreciable degree but are invariably poorly mineralized.

(*c*) *Quartz-mica veins.*—These occur only in the schists and gneisses and are always smaller than the average felspathic pegmatite. They are composed of coarse muscovite and glassy quartz and sometimes contain

[1] R. Jacobson and J. S. Webb, The pegmatites of central Nigeria. Bull. Geol. Surv. Nigeria, 1946, no. 17.

cassiterite, columbite-tantalite, and other accessory minerals. The mica is orientated roughly perpendicular to the walls of the vein.

A quartz-mica marginal facies is commonly present on the walls of the microcline-quartz-muscovite-pegmatites, especially on the hanging-wall.

## IV. Quartz-sillimanite-rocks containing nigerite.

Quartz-sillimanite-rocks containing nigerite have been found at the following localities:

(*a*) *M.L.*[1] *4429*: Three miles south-east of Oke Oloke, and about two miles from the contact of the Egbe Older Granite.

(i) A large quartz-sillimanite vein which has been worked for cassiterite.

(ii) A subordinate quartz-sillimanite facies associated with the quartz-mica margin of a large albitized microcline-quartz-muscovite-pegmatite 250 yards west-north-west of (*a*).

(iii) Several small quartz-sillimanite veins.

(*b*) *Old M.L. 712*: About two miles east of (*a* i). A large albitized microcline-quartz-muscovite-pegmatite with a well-developed quartz-sillimanite facies associated with the quartz-mica margin on the hanging-wall.

(*c*) *Old tin-workings three-quarters of a mile east of Isanlu Isa*: A large albitized microcline-quartz-muscovite-pegmatite which has been worked for cassiterite. The quartz-sillimanite-rock was found in the spoil heaps but was not noted in situ.

(*d*) *M.L. 5083*: South-east of Bakin Kogi. Several intensely albitized pegmatites have been worked for cassiterite on this lease. A few small pieces of the quartz-sillimanite-rock were found in the spoil heaps, but the rock was not seen in situ.

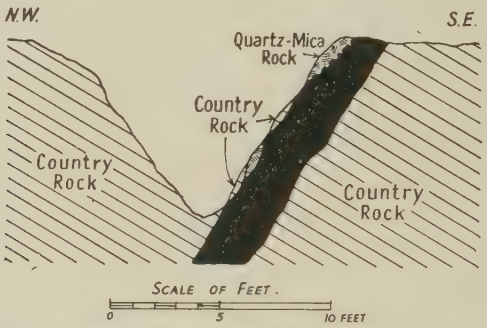
Of these, (*a* i) and (*b*) are by far the best and most interesting exposures. It is perhaps worth recording that a quartz-sillimanite vein containing andalusite, garnet, and chrysoberyl has been found recently near Hoss 200 miles to the north of the Egbe area.[2]

(*a*) *M.L. 4429*, (i) *Quartz-sillimanite vein.*—This vein (text-fig. 2) is 18–30 inches wide and outcrops over a distance of 200 feet; old tin-workings, however, indicate that it is probably at least 600 feet long. The vein strikes N. 50° E., dipping at an angle of 40–60° to the NW. Except for minor irregularities, the walls are smooth and the contact with the country-rock appears to be sharp, but weathering is too extensive for accurate observations or even to determine the precise nature of the country-rock. A most important feature is the development, in places, of a quartz-mica marginal facies which resembles closely the quartz-mica margins of some of the felspathic pegmatites and also the quartz-mica veins.

[1] M.L. is the abbreviation for 'Mining Lease'.

[2] R. Greenwood, Geology of the plateau tinfields. Interim Report Geol. Surv. Nigeria, 1945, no. 1.

The quartz-sillimanite-rock is extremely hard and tough. Quartz is abundant, and, in addition to the massive type common to these deposits, there is a very fine-grained sugary variety. Much sillimanite occurs as sheaf-like aggregates of fibrolite. Locally, andalusite, often pink in colour, becomes an abundant constituent. In addition to the normal white muscovite of the quartz-mica marginal facies, there is a very subordinate silvery-white mica distributed sparingly through the vein. Other accessory minerals include: (*a*) garnet, in segregations up




TEXT-FIG. 2. Diagrammatic section across a nigerite-bearing quartz-sillimanite vein (black). Note the discontinuous quartz-mica facies on the hanging-wall. (Locality: M.L. 4429, 3 miles north-east of Barbella Hill.)

to 4 inches in diameter, (*b*) dark brown cassiterite, and (*c*) the green spinel, gahnite. All these are scattered irregularly throughout the rock, but gahnite may be concentrated in narrow bands parallel with the walls of the vein. Nigerite, though unevenly distributed, is sometimes locally abundant and is often associated and intergrown with gahnite, often as a coating on the crystal faces. Generally it occurs as isolated brown hexagonal plates up to $\frac{3}{8}$ inch in diameter. Pale yellow tabular crystals of chrysoberyl are not uncommon.

*M.L. 4429*, (ii) *Quartz-sillimanite facies associated with the quartz-mica margin of an albitized felspathic pegmatite.*—A 6-feet wide microcline-quartz-muscovite-pegmatite outcrops about 250 yards WNW. of the vein mentioned above, trending in the same direction. The outcrop is about 300 feet long but extends some way to the SW. along the line of some old workings. A narrow band of quartz-sillimanite-rock, containing andalusite and a little nigerite, was observed associated with the quartz-mica marginal facies. This latter rock is well developed on the hanging-wall, and the quartz-sillimanite band appears to occur between the

quartz-mica zone and the country-rock. Spoil heaps in the old workings indicate that the quartz-sillimanite facies was also present in that part of the dike which was worked for cassiterite. The felspathic core of the pegmatite contains abundant fine-grained albite, with which the bulk of the cassiterite was probably associated—the normal association in these tin-bearing pegmatites (Jacobson and Webb, 1946, loc. cit.).

*M.L. 4429*, (iii).—Traces of nigerite were also found in several smaller quartz-sillimanite veins on this lease; these veins vary from 2 inches to 1 foot in width.

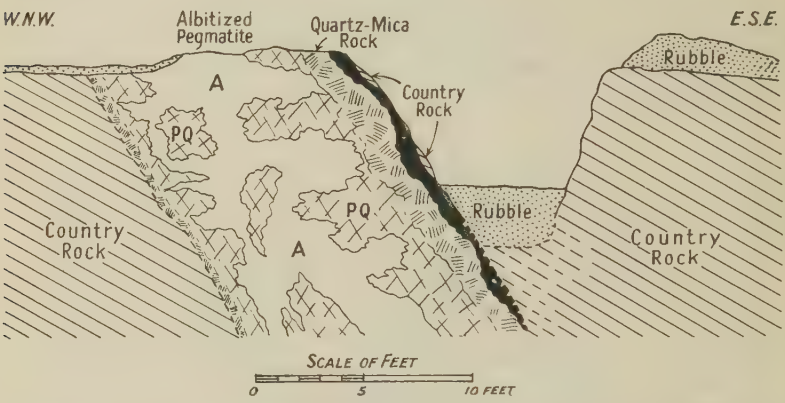
Other veins in the same locality include (*a*) quartz-mica veins, (*b*) quartz veins, and (*c*) a quartz vein carrying a little sillimanite and ilmenite. Stream concentrates in the vicinity contain a little gold.

(*b*) *Old M.L. 712.*—A large dike of albitized microcline-quartz-muscovite-pegmatite, which has been worked for cassiterite, outcrops on this lease. The dike is exposed for 600 feet along the strike, but prospecting trenches indicate that it continues for several hundred yards to the SSE., the strike direction being S. 23° E. The dip is variable, 30–60° to the ESE. As the foot-wall is not exposed, it was not possible to determine the width, which probably exceeds 10 feet. On the hanging-wall of this dike, there is a 16-inch quartz-mica margin which grades into a quartz-sillimanite facies. This latter zone varies from an inch or so to about one foot in width, and is not always present. The bulk of the nigerite occurs in this quartz-sillimanite band; a little nigerite and gahnite are also present in the quartz-mica margin near the quartz-sillimanite-rock. The relationship with the country-rock is not fully exposed (text-fig. 3), but it is probable that the quartz-sillimanite facies occurs on the contact.

The felspathic core of the pegmatite contains abundant fine-grained albite, microcline-perthite, quartz, and muscovite. Garnet, cassiterite, and other accessory minerals are also present. The quartz-sillimanite facies is similar to that described above. Again, nigerite is distributed irregularly and is sometimes associated and intergrown with gahnite and muscovite. Chrysoberyl is not uncommon. It is significant that nigerite and gahnite also occur sparingly in the quartz-mica facies.

(*c*) *Old tin-workings three-quarters of a mile east of Isanlu Isa.*—A few lumps of quartz-sillimanite-rock were observed in the spoil heaps around an albitized microcline-quartz-muscovite-pegmatite which has been worked for cassiterite. A little nigerite and chrysoberyl occur in the quartz-sillimanite facies. Garnet and cassiterite are also present.

(*d*) *M.L. 5083.*—Two albitized microcline-quartz-muscovite-pegmatites have been worked on this lease. A few small pieces of the quartz-sillimanite-rock were observed in the spoil heaps. A little nigerite is present.




TEXT-FIG. 3. Diagrammatic section across a complex dike on old M.L. 712, 4 miles north of Oke Iromo. Most of the dike is composed of coarse microcline-perthite-quartz-pegmatite (PQ) veined and replaced by later fine-grained albite-quartz-rock (A). A quartz-mica band is well developed on the hanging-wall in contact with the marginal facies, which is a nigerite-bearing quartz-sillimanite-rock (black).

## V. MINERAL ASSOCIATIONS.

The following lists show the mineral associations in the nigerite-bearing rocks and also a connexion between them and the pegmatite suite:

| I. Quartz-sillimanite-rock. | II. Quartz-mica-rock. | III. The common quartz-mica facies of the pegmatite suite. |
|---|---|---|
| Nigerite | Nigerite | Quartz |
| Quartz | Quartz | Muscovite |
| Sillimanite | Muscovite | Gahnite |
| Andalusite | Gahnite | Garnet |
| Gahnite | Garnet | Cassiterite |
| Garnet | Cassiterite | Columbite-tantalite |
| Chrysoberyl | Apatite | Beryl |
| Cassiterite | | Apatite |
| Columbite-tantalite | | Tourmaline |
| Silvery-white muscovite | | |
| Apatite | | |

### (*a*) *Nigerite.*

The new mineral nigerite occurs as shiny dark-brown, hexagonal plates up to $\frac{3}{8}$ inch in diameter. In the hand-specimen it has an

appearance similar to that of thin, well-formed biotite flakes, but it is extremely brittle. Nigerite is feebly magnetic.

Basal sections are rare in thin section and nigerite is usually seen as pale brownish-yellow laths with a high relief. The laths are frequently traversed by cracks which rarely continue into the adjacent minerals. There is also a definite, though feeble, basal cleavage or parting. Crystal form is usually well developed except where displacement or 'faulting' has been caused by a post-crystallization movement. No corrosion or replacement by other minerals has taken place. Occasionally one crystal cuts across another to form a cross (pl. VI, fig. 4). Faint, patchy pleochroism is sometimes visible, $\epsilon$ pale brownish-yellow, $\omega$ slightly darker brownish-yellow. Basal sections, which are generally hexagonal, give a positive uniaxial figure. The birefringence is low.

Inclusions are rare and appear to be mainly quartz, though they are too small to be positively identified. Nigerite crystals are frequently surrounded by a dense mat of fine sillimanite fibres (fibrolite). In one section it is found growing on the surface of gahnite crystals, and a wedge of nigerite has been seen penetrating the gahnite. An octahedron of the latter mineral completely covered by a coating of nigerite was collected from the same locality. This relationship is quite common. Muscovite has been noted intergrown with and penetrated by crystals of nigerite (pl. VI, fig. 5).

(*b*) *Associated minerals.*

*Quartz* is the most abundant constituent of the rock, and is present as an allotriomorphic mosaic of interlocking grains, which occasionally show evidence of strain. The grain-size varies considerably. It is colourless, but frequently appears to be milky owing to disseminated fine needles of sillimanite. Occasionally it encloses nigerite, cassiterite, chrysoberyl, &c. Quartz replaces andalusite extensively (pl. VI, fig. 6).

*Sillimanite* is present mainly as a mat of extremely fine fibres (fibrolite) which is brownish-grey in thin section (pl. VI, figs. 1 and 3). Occasionally it occurs as discrete crystals. It is commonly found around nigerite and cassiterite, and has also been noted surrounding garnet and residual pools of andalusite. As mentioned before, quartz is frequently riddled with needles of sillimanite, which may be arranged irregularly, in parallel orientation, or in radiating aggregates. Where quartz is replacing andalusite, any sillimanite present is confined to the quartz.

*Andalusite* originally crystallized as occasional segregations of large, pale-pink crystals; these have since been extensively replaced by quartz (pl. VI, fig. 6) and now occur as scattered, optically continuous relics. In

some specimens andalusite apparently composed the bulk of the rock before replacement. It is usually colourless in thin-section, though when pleochroism is visible it is colourless to pale-pink. The replacing quartz may contain associated wisps of white mica, and fibrolite sometimes surrounds residual pools of andalusite.

*Muscovite*, occurring as 'books' up to $\frac{1}{2}$ inch in diameter, is one of the major constituents in the nigerite-bearing quartz-mica-rocks. In sections from the quartz-sillimanite facies, however, it can only be found as subordinate interstitial wisps and flakes. In both cases it is always closely associated with quartz. Broadly speaking, sillimanite and muscovite show a tendency to be mutually exclusive in these rocks containing nigerite.

*Gahnite* is a characteristic constituent. It is invariably dark-green and occurs as irregular grains to perfect octahedra up to $\frac{1}{4}$ inch in diameter. Gahnite contains inclusions of quartz and is often coated and intergrown with nigerite.

*Garnet* forms segregations up to 4 inches across and individual euhedral crystals $\frac{1}{2}$ inch in diameter have been found. The garnet is red-brown in colour and is essentially free of inclusions. It is generally enclosed in quartz but may be surrounded by a zone of fibrolite. Decomposition has produced iron and manganese oxides, which fill cracks in the mineral and may also occur as a dendritic halo surrounding the crystal. The garnet is probably a spessartine-almandine, which is the characteristic garnet of the pegmatite suite.

*Cassiterite* occurs as irregular crystals and aggregates. As with most of the Nigerian pegmatite tinstone, it is zoned and intensely pleochroic in blood-red and brown; twinning is a common feature. Inclusions are plentiful and consist mainly of quartz and columbite-tantalite. Occasionally the textural relationship between cassiterite and quartz indicates replacement by quartz (pl. VI, fig. 2). Its relationship to nigerite is obscure: both are usually surrounded by fibrolite, but the cassiterite rarely shows good crystal form (pl. VI, fig. 3) and often contains inclusions, thereby differing considerably from nigerite in both respects.

*Columbite-tantalite* is present as small, black rods and grains (pl. VI, figs. 2 and 3). The tabular crystal form, as shown by a series of cross-sections, resembles the habit of the coarser columbite-tantalite found in the associated felspathic pegmatites and quartz-mica veins. Furthermore, some grains show deep red-brown, translucent edges possessing a high relief, and are pleochroic. Columbite-tantalite occurs enclosed in cassiterite and nigerite. It is most commonly concentrated in quartz

near cassiterite, often surrounded by fibrolite. In one slide, a crystal of columbite-tantalite was seen penetrating slightly into a euhedral crystal of chrysoberyl.

*Chrysoberyl* is present in the quartz-sillimanite-rocks as good platy crystals up to 1½ inches long (pl. VI, fig. 3). It is colourless to pale yellow, contains no inclusions and has not been affected by replacement. Chrysoberyl occurs enclosed in quartz and occasionally surrounded by a zone rich in sillimanite. A few crystals have been seen coated with nigerite.

*Apatite* is very subordinate, though widespread, and forms irregular pools of poorly shaped crystals in quartz.

## IV. Paragenesis.

A detailed paragenesis for the constituents of the nigerite-bearing quartz-sillimanite-rocks has not been attempted in view of the restricted nature of the field exposures and the consequent inadequate number of critical specimens. The available material, however, has provided sufficient data to justify certain interesting conclusions. A study of the relationships between the various mineral constituents shows that:

(*a*) Andalusite was one of the earliest minerals and is replaced to a considerable degree by quartz.

(*b*) Sillimanite formed after andalusite. The occurrence of fibrolite around residual pools of andalusite indicates that at least some of the alumina for sillimanite may have been acquired at the expense of andalusite.

(*c*) Garnet, chrysoberyl, gahnite, columbite-tantalite, nigerite, and cassiterite, all started to crystallize before most of the sillimanite. It is possible also that they started to crystallize in the order given, but there was considerable overlap in most cases. The position of columbite-tantalite relative to cassiterite, nigerite, and sillimanite is established.

(*d*) Gahnite started to crystallize before nigerite, and nigerite continued to be deposited after gahnite had ceased to form, often as orientated overgrowths on the latter.

(*e*) Where muscovite is present in any quantity, sillimanite is either absent or subordinate. The concentration of potash in the solutions may have been one of the governing factors.

## V. Conclusion.

The nature of the available field exposures is not conducive to a complete interpretation of the origin of these interesting nigerite-bearing

rocks. However, the field relationships and mineral assemblages prove the existence of a close connexion with the stanniferous pegmatite suite in Nigeria. It is probable that the nigerite-bearing rocks are the result of a peculiar and unusual phase of pegmatite development.

It is hoped that it will be possible to continue the investigation of these deposits with a view to obtaining further critical evidence concerning their genesis.

### Explanation of Plate VI.

Photomicrographs of nigerite in quartz-sillimanite-rocks from Nigeria.

Ordinary light. C cassiterite, Ch chrysoberyl, CT columbite-tantalite, F fibrolite, M muscovite, N nigerite, Q quartz. (Photomicrographs by J. A. Gee, Royal School of Mines, London.)

Fig. 1. A typical section showing crystals of nigerite surrounded by dense mats of fibrolite in clear quartz. The laths of nigerite are transverse sections of hexagonal, platy crystals. ×10.

Fig. 2. Nigerite, sillimanite, and quartz are seen surrounding a large crystal of dark-brown cassiterite, which is somewhat replaced by quartz. Small black rods and grains of columbite-tantalite are disseminated in the quartz surrounding the cassiterite, and a few grains can be seen enclosed in the latter. ×20.

Fig. 3. A segregation of fibrolite, nigerite, and cassiterite in clear quartz. Small grains of columbite-tantalite and a large crystal of chrysoberyl are included. ×10.

Fig. 4. A cruciform growth of two crystals of nigerite in fibrolite and clear quartz. Note the concentration of fibrolite around the nigerite. ×32.

Fig. 5. A large dark nigerite crystal penetrates a crystal of muscovite. Both minerals are replaced by a tongue of clear quartz. ×22.

Fig. 6. A single crystal of andalusite (high relief) partially replaced by a mosaic of clear quartz grains. The smudgy dark areas represent dense fibrolite, which is actually translucent but the negative was under-exposed to capture the quartz-andalusite relationship. ×11.